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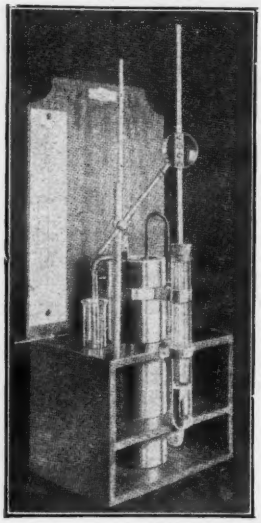

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THE INFLUENCE OF CALCIC AND MAGNESIC ADDITIONS UPON THE OUTGO OF SULFATES FROM A LOAM SOIL AS MEASURED BY LYSIMETER LEACHNGS OVER AN 8-YEAR PERIOD

W. H. MacINTIRE, W. M. SHAW AND J. B. YOUNG[1]

University of Tennessee Agricultural Experiment Station

Received for publication March 5, 1923

INTRODUCTORY

The subject of soluble soil sulfates is one of importance. Field lysimeters probably afford the best opportunity to study the occurrence of such salts, their availability under different conditions, and the progress of sulfofication. The few available lysimeter data on sulfate leachings have been compiled by Lyon and Bizzell (2, p. 77) and will not be cited here. Unqualified application of such results is hardly permissible, since only those cited from Von Seelhorst were secured from experimentation extending beyond periods of a few months, which intervals we will show constitute the period of initial abnormality in sulfate outgo.

The results to be offered in this contribution constitute a study of the formation of sulfates and subsequent acceleration or retardation of leaching, as influenced by different forms and varying amounts of calcic and magnesic materials. The investigation also included a study of the balance between sulfur precipitation in rainfall and loss through leaching. The leachings were all from fallow soil, thus avoiding the influence of plant growth. The duplication of treatments in surface soil alone and in surface soil underlaid by subsoil afforded opportunity for determination of the function of the subsoil in changing the sulfate concentration of the leachings from the surface soil. In this regard the investigation may be considered as distinctive. In so far as we are aware, it is also without parallel in scope of comparisons and magnitude of treatments, nine different calcic and magnesic materials being used, with an upper limit of 100 tons of CaO, or its equivalent, per acre.

EXPERIMENTAL

The experimental results were obtained during an 8-year study with 46 field lysimeters each 1/20,000 acre in area. The experimental period ex-

[1] Much of the earlier analytical work in this investigation was done by Messrs. L. G. Willis, W. A. Holding and F. J. Gray, formerly of the Tennessee Agricultural Experiment Station.

tended from July 15, 1914, to July 15, 1922. The soil used is a Cumberland loam of the Hagerstown series and was obtained from a nearby source. It was so protected as to maintain a condition close to the optimum of moisture content throughout the processes of screening, mixing to insure uniformity and the working in of additions. Each tank received the equivalent of 100 pounds of moisture-free soil. The treatments were CaO, MgO, $CaCO_3$, $MgCO_3$, 100-mesh limestone, 100-mesh dolomite and 100-mesh magnesite, each at the *CaO equivalent* rate of 8 tons, 32 tons, and 100 tons per 2,000,000 pounds of soil. Wherever used in the text in connection with these seven treatments the three terms *8-ton*, *32-ton* and *100-ton* are intended to express

TABLE 1

Composition of soil and materials used for treatments

LABORATORY NUMBER	MATERIAL	SiO_2	Fe_2O_3 AND Al_2O_3	CaO	MgO	CO_2	$CaCO_3$	$MgCO_3$	SO_3
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
3216	CaO	0.10	0.53	97.15§	0.87	0.13	0.30	0.00	0.00
3222	MgO	0.27	0.00	2.58	90.10	1.29	0.00	2.47	0.25
3220	$CaCO_3$	0.18	0.00	54.93	0.38	43.09	98.09	0.80	0.26
3221	$MgCO_3$*	0.31	0.00	0.00	43.38	35.50	0.00	68.04	0.15
3217	Limestone	2.45	0.85	52.83	0.78	42.57	94.33	1.49	0.00
3218	Dolomite	9.66	1.00	27.98	18.70	40.98	49.96	35.70¶	2.33
3219	Magnesite	1.94‡	0.28	0.00	47.53	50.45‖	0.00	96.68‡	0.14
3227	Wollastonite	....	....	45.11	0.48	0.69	1.57	0.00	0.06
3228	Serpentine	....	....	0.09	37.79	0.14	0.00	0.27	0.28
3343	Soil†	....	....	0.18	0.30	.....	.....	.....	0.1060
3224	Subsoil†	....	....	0.19	0.47	.....	.....	.....	0.0840

* Analysis calculates to formula, $3\,MgCO_3 \cdot Mg(OH)_2 \cdot 3\,H_2O$ plus 3.25 per cent moisture.
† Carbonate fusion.
‡ $MgSiO_3$, 3.24 per cent.
‖ By difference.
¶ Most probably some $MgSiO_3$ present.
§ Contained 5.84 per cent $Ca(OH)_2$.

equivalence of CaO. The analyses of the calcic and magnesic materials are given in table 1. The primary object of the experiment was a study of alkali-earth absorption, hence, the range in treatments up to excessive amounts. The effect of treatments as low as one ton of CaO, or its equivalent, will be considered in another paper. All treatments were mixed throughout the entire amount of soil. Each treatment was made to a tank which had 8 inches of surface soil and no subsoil and also to a tank which contained the same amount of surface soil and one foot of red clay subsoil. The surface soil tanks will also be referred to as shallow tanks; the subsoil tanks, as deep tanks. In addition, one of the deep tanks received 100-mesh wollastonite at the rate of 32 tons per 2,000,000 pounds of soil and another received 100-

mesh serpentine at the same rate. Fitting in the original scheme, the two silicate tanks were included instead of no-treatment controls. The untreated controls 45 and 46 were installed after the second year. The average annual losses are therefore determined by division by 6 in the case of the controls and by 8 in the case of treatments. No addition of sulfur was made to any of the tanks, save as treatment impurities and that which was carried by the natural rainfall. The sulfate precipitations over the same 8-year period have been reported (7). A preliminary contribution (8) has been offered, showing the divergent effects of calcium and magnesium during the first two years of the 8-year priod. The field lysimeter equipment has also been described (4, p. 6–8; 6). The analyses for sulfate outgo were made upon each of the eight annual composites, and are given in tables 3, 4 and 5. The sulfate determinations were all made gravimetrically, in duplicate, with a 2 mgm. analytical limit of variation. This analytical limit of error is equivalent to 3.8 pounds of SO_3 per acre per annum from a representative leaching of 125 liters per tank.

AMOUNTS OF SULFUR CONTAINED IN SOIL, TREATMENTS, AND RAINFALL

The amount of sulfur present in each of the several containers was not a constant, because of the variation in the sulfur carried by the different treatments and because of the several rates of addition. The subsoil tanks contained greater quantities of sulfur than the corresponding tanks which had only the surface soil. The SO_3 content of surface soil was found to be 0.1060 per cent and that of subsoil 0.0840 per cent. The total sulfur occurrences in soil and subsoil were obtained by oxidation with sodium peroxide. The studies leading to perfection of the method and the details of manipulation will be given in another contribution. A 3-hour agitation of 20-gm. charges in 150 cc. of water gave SO_3 occurrences of 0.0152 per cent and 0.0185 per cent for soil and subsoil, respectively. The earlier contribution on rainfall sulfur showed the abnormal precipitation over the 8-year period of experimentation to be practically one-half of that contained by the soil at the beginning of the experiment. The total sulfur supply of each tank, as represented by the composition of soil, subsoil, treatment-impurities, and the atmospheric precipitation, is given in table 2.

THE SULFATE CONTENT OF LEACHINGS

The sulfate losses from the additions of calcic and magnesic materials, as determined by the leaching analyses, will be considered under four headings:

(1) *Comparison between treatments* in each 7-unit group with reference to the divergent effect of calcium and magnesium in materials of varying form and solubility and with variation in soil depth, without regard to source of sulfur.

(2) *Effect of each separate material* as it may vary with the magnitude of addition and with soil depth, without consideration of the source of sulfur.

(3) *Comparison between treatments* in each 7-unit group as showing the relationships between (A) losses and the sulfur derived from each source and (B) losses and the aggregate of all sulfur supplies.

TABLE 2

Possible sources of sulfates in leachings. Amounts of SO_3 in loam soil, subsoil, alkali-earth treatments and in the 8-year precipitation

TREATMENT	SO_3 IN SOIL		SULFATE IN 8 YEARS' RAINFALL	SO_3 AVAILABLE PER ACRE FROM SOIL CONSTANT, RAINFALL CONSTANT AND TREATMENT VARIABLE					
				8-ton treatment		32-ton treatment		100-ton treatment	
	Surface soil	Subsoil		As impurities in treatment	Total from all sources	As impurities in treatment	Total from all sources	As impurities in treatment	Total from all sources
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
CaO	2120	....	1029	0	3149	0	3149	0	3149
CaO	2120	2772	1029	0	5921	0	5921	0	5921
MgO	2120	....	1029	30	3179	120	3269	375	3524
MgO	2120	2772	1029	30	5951	120	6041	375	6296
$CaCO_3$	2120	....	1029	72	3221	288	3437	900	4049
$CaCO_3$	2120	2772	1029	72	5993	288	6209	900	6821
$MgCO_3$	2120	....	1029	37	3186	148	3297	463	3612
$MgCO_3$	2120	2772	1029	37	5958	148	6069	463	6384
Limestone	2120	....	1029	0	3149	0	3149	0	3149
Limestone	2120	2772	1029	0	5921	0	5921	0	5921
Dolomite	2120	....	1029	701	3850	2804	5953	8763	11912
Dolomite	2120	2772	1029	701	6622	2804	8725	8763	14684
Magnesite	2120	....	1029	33	3182	132	3281	413	3562
Magnesite	2120	2772	1029	33	5954	132	6053	413	6334
Wollastonite	2120	2772	1029	..	....	40	5961†	....	....
Serpentine	2120	2772	1029	..	....	180	6101†	....	....
None‡	2120	....	772*	..	....	....	....	....	....
None‖	2120	2772	772*	..	....	....	....	....	....

* Six years.

† Actual rate of 32 tons of material.

‡ Total, 2892 pounds.

‖ Total, 5664 pounds.

(4) *Effect of such separate material* as showing the influence of rate of treatment and relation of sulfate outgo to each partial source and the total of all sulfur present.

EIGHT-TON TREATMENT

Surface-soil tanks

Increased outgo of sulfates from the surface soil was induced by all of the calcic and magnesic additions at the 8-ton rate during the initial year, as will be seen by reference in table 3. The outgo from each treatment was in excess of the water soluble sulfate content of the dry reserve sample. It is most probable that this increase was due chiefly to acceleration in bacterial activities, although it might be contended that the added materials served to reduce the soil's physical ability to retain sulfates. The minimum amount

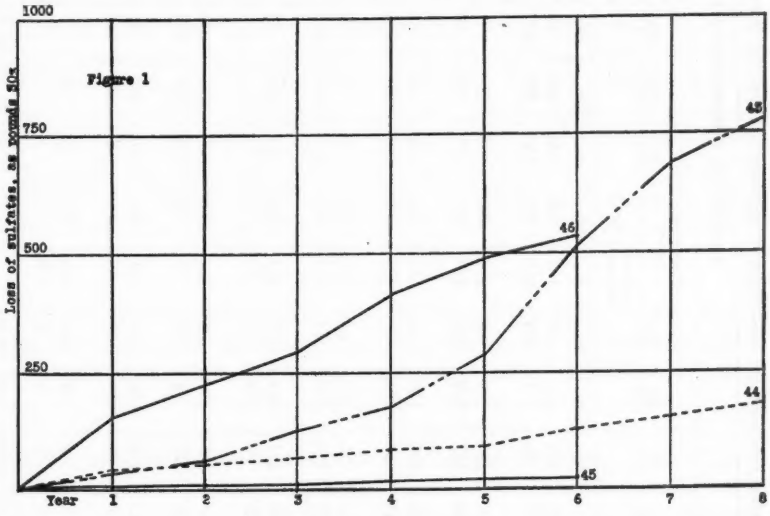

FIG. 1. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM CONTROLS AND SILICATE TANKS

Tank 43—32 tons wollastonite, soil-subsoil
44—32 tons sepentine, soil-subsoil
45—control, soil-subsoil
46—control, surface soil only

of 341 pounds of SO_3 resulted from the burnt lime treatment and the maximum of 540 pounds, from the limestone addition. This maximum for the initial year was more than equivalent to the total outgo from the shallow-tank control for the 6-year period. The initial annual sulfate loss from both magnesium carbonate and magnesite was practically equivalent to the 6-year aggregate outgo from the control tank. Magnesium oxide proved more active than calcium oxide in accelerating the leaching of sulfates. The precipitated carbonate of magnesium was also more active than the corresponding form of calcium. As compared with the first year's results, there was a decided

TABLE 3

Sulfate content of leachings from loam soil with treatments equivalent to 8 tons CaO per acre

TANR NUMBER	TREATMENT	AS TO SUBSOIL	TOTAL VOLUME OF LEACHINGS	SO_3 LEACHED PER 2,000,000 POUNDS OF SOIL													
				1st year	2d year	3rd year	4th year	First 4-year period		5th year	6th year	7th year	8th year	Second 4-year period		Whole 8-year period	
								Annual average	Total					Annual average	Total	Annual average	Total
			liters	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
1	CaO	None	991	341	267	112	67	197	787	108	106	66	37	79	317	138	1104
22	CaO	Clay	1060	33	68	197	101	100	399	166	229	132	66	148	593	124	992
2	MgO	None	979	469	141	119	67	199	796	100	119	67	36	81	322	140	1118
23	MgO	Clay	1021	40	162	269	126	149	597	153	215	130	55	138	553	144	1150
3	$CaCO_3$	None	1009	468	203	140	87	225	898	108	111	68	37	81	324	153	1222
24	$CaCO_3$	Clay	1073	35	58	222	82	99	397	253	280	138	65	184	736	142	1133
4	$MgCO_3$	None	1076	528	170	102	63	216	863	100	110	79	37	82	326	149	1189
25	$MgCO_3$	Clay	1011	32	136	330	113	153	611	163	203	115	54	134	535	143	1146
5	Limestone	None	1044	540	214	119	68	235	941	112	109	59	40	80	320	158	1261
26	Limestone	Clay	1024	20	29	190	82	80	321	153	239	149	69	153	610	116	931
6	Dolomite	None	950	402	215	130	101	212	848	139	134	99	51	106	423	159	1271
27	Dolomite	Clay	1024	21	27	92	54	49	194	134	224	162	79	150	599	99	793
7	Magnesite	None	1038	512	171	126	76	221	885	110	109	65	37	80	321	151	1206
28	Magnesite	Clay	973	31	36	99	52	55	218	136	244	152	65	149	597	102	815
46	None	None	838*	155	66	68	126	104	415	73	46	...	...	60	...	89	534*
45	None	Clay	777*	6	3	1	9	5	19	3	2	...	...	3	...	4	24*
Inches of rainfall				47.78	56.54	63.32	47.79	...	...	51.41	54.21	50.37	55.63	...	...	...	....

*Six years.

decrease in sulfates leached from all treatments during the second year and further progressive decreases during the third and fourth years. The initial 4-year totals show a minimum of 787 pounds for the CaO treatment and a maximum of 941 pounds for the limestone addition. The totals and average annual losses for the five carbonate treatments are grouped rather closely and are considerably greater than the corresponding results from the two oxide additions. As compared with the fourth year's results, leached sulfates increased somewhat during the fifth and sixth years. The losses for those two years are almost duplicated for each respective treatment, though the rainfall of the sixth year was considerably greater than that of the fifth. Again, during the seventh and eighth annual periods, there was a consistent decrease. This very definite tendency toward eventual decreases in sulfate outgo would naturally be expected to follow the depletion of the soil's native store of sulfur materials. The 8-year totals are in harmony with those of the first 4-year period in showing the two oxide tanks as trailing the remaining five carbonate treatments. The totals from the limestone and dolomite treatments are very close, that from the dolomite being the maximum outgo for the full 8-year period. The two precipitated carbonates come next in order, with rather close grouping.

Surface-soil and subsoil tanks

In contrast with the surface-soil tanks, those of the subsoil series yielded the smallest amount of sulfates during the initial year. During the second and third years a material increase is noted, especially in the case of the magnesium oxide and carbonate treatments, which induced a fourfold increase in outgo during the second year. The maximum annual loss of the first 4-year period was obtained from all seven treatments during the third year which was one of abnormal rainfall. Following the uniform drop of the fourth annual period every treatment gave an increase in the fifth year, followed by a still further increase the sixth year. After the large losses of the sixth year, consistent decreases in outgo were observed for all treatment during the seventh year, and a still further decrease during the eighth and final year.

It will be noted that each addition has very materially increased the outgo of sulfates over the several meager annual losses—a maximum of 9 pounds from the no-treatment deep tank. Each treatment has been responsible, therefore, for either an enhanced movement of sulfates from the soil and through the subsoil, or a change in the retentive properties of the subsoil, unless it be that calcic and magnesic salts have caused an increased formation of sulfates within the subsoil—a less probable alternative for these particular conditions. It may be assumed with reason that the processes of sulfofication were essentially the same in the treated surface soil, whether underlaid by a sand filter bed or by subsoil. If this be true, it is apparent that even though permitting the passage of part of the sulfates which came from the surface soil, the subsoil depth of one foot has arrested an average

*Six years.

of 445.4 pounds of SO_3 during the initial year. This tendency to stop the downward movement of sulfates diminished in time in the case of additions but not in the control. The more soluble additions were responsible for larger amounts of the alkali-earth bases passing down to the subsoil and, coincident with this greater downward movement of bases, there occurred

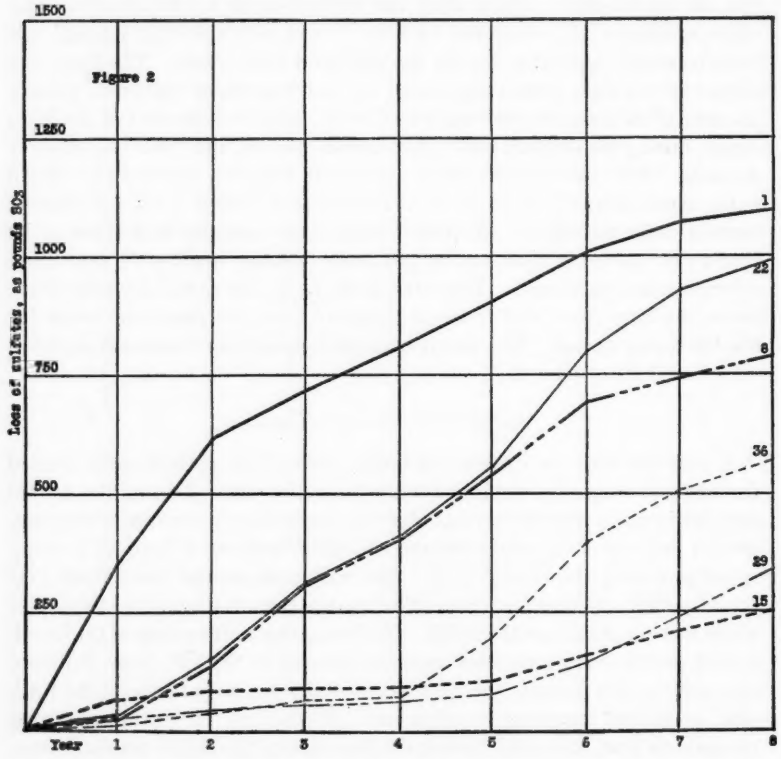

FIG. 2. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH CaO AS FOLLOWS:

Surface soil	Tank 1— 8 tons	Surface and subsoil	Tank 22— 8 tons
	8— 32 tons		29— 32 tons
	15—100 tons		36—100 tons

a diminished tendency toward sulfate retention. Parallel determinations of occurrences of sulfate sulfur, calcium, and magnesium in the leachings demonstrated that the sulfate absorption is a molecular one, for no marked increase of sulfates occurred in the leachings until increases of calcium and magnesium were also found. The consistent gain in the sulfate yields from subsoil tanks which contained the four oxide and precipitated carbonate

treatments brought the 8-year average proportion for the calcium additions up to more than 91 per cent of the surface soil outgo and that of the magnesium additions to 99.5 per cent. In the case of the three less soluble natural carbonates, however, the lag in the total sulfate outgo from the deep tanks was still very marked, though the amounts leached through the subsoil tanks during the last four years were greater than those from the corresponding surface soil tanks in every instance save one. Hence, after 8 years of leaching, only about 68 per cent of the surface-soil sulfate yield had been found in the subsoil tank leachings, as the average from the limestone, dolomite, and magnesite treatments.

It is therefore established that all of the seven calcic and magnesic materials were responsible for a very extensive acceleration in movements of sulfates from the surface soil. It is also apparent that marked variations in the solubilities of the several materials and sulfate end-products were responsible for wide differences in the amounts of leached sulfates, where the absorptive properties of the subsoil were brought into play. On the other hand, it will be noted that during six years a total difference of over 500 pounds of sulfate outgo obtains between the leaching of 534 pounds from the surface soil and that of 24 pounds from the soil-subsoil. It is evident, therefore, that a marked retentive property is inherent in the subsoil, which has not been subjected to the ameliorating influence of additions of either of the alkali-earth elements. Though the amounts of sulfates leached from the surface soil control and that from the subsoil control are decidedly less than the amounts obtained from any one of the corresponding treated tanks, it is most probably true that the outgo from each control is abnormal because of enhanced sulfofication as a result of the thorough aeration incident to digging, screening, and mixing of the moist soil at the beginning of the experiment. Were such extensive sulfate generations and leachings to occur, with no replacements through additions and atmospheric precipitations, the loss of the native stores of sulfur in the surface soil would soon become a fertility factor.

Comparison with Cornell experiments. The results from the 8-ton series especially may be considered in connection with the results obtained from 3000 pounds of CaO by Lyon and Bizzell (2, p. 73). From leachings during a 5-year period from a 4-foot depth of Dunkirk soil, rather high in its CaO content, particularly in the lower zones, these investigators found evidence that lime caused enhancement in sulfofication. It is difficult, however, to determine from which zone or zones the sulfates were derived in the experiments of Lyon and Bizzell, where only the 4-foot depth was used. The sulfate totals and disparity between control and treatment were but fractions of those found by us in our lightest treatment. In a later report (3, p. 73) parallel data are given for a Volusia soil of decidedly less CaO content in each of four 1-foot zones. In this case no evidence was given to show increase of sulfate formation from the addition of lime although increased nitrate outgo was shown. They concluded: "Liming the Dunkirk soil did not re-

sult in an increased formation of nitrates, but apparently favored sulfofication. Application of lime to the Volusia soil was accompanied by increased nitrification, but had no effect upon the production of sulfates. This would indi-

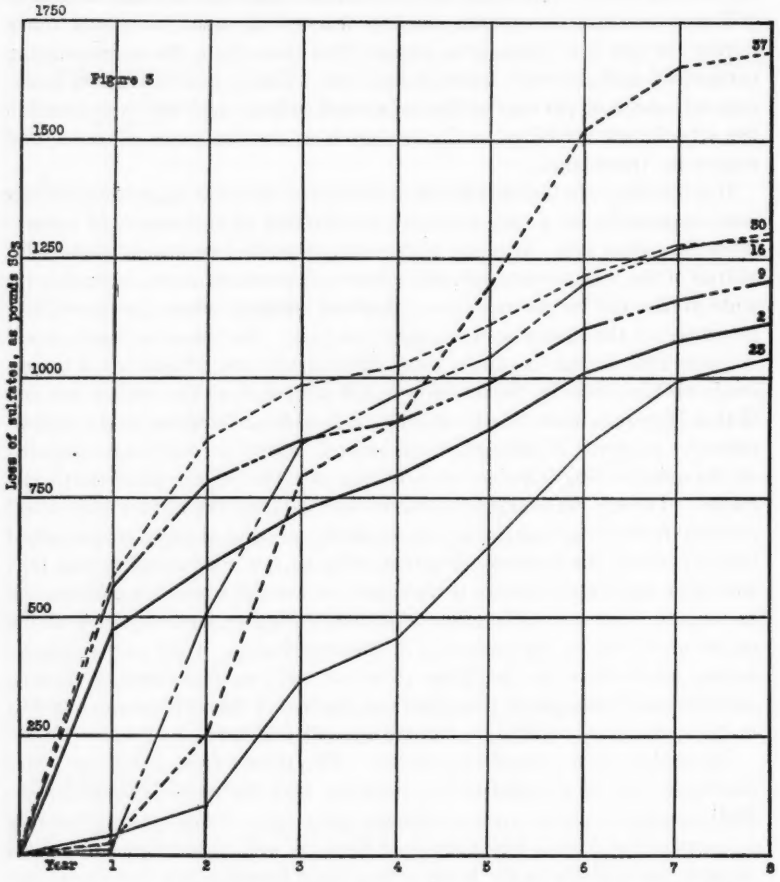

FIG. 3. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH MgO EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 2— 8 tons	Surface and subsoil	Tank 23— 8 tons
	9— 32 tons		30— 32 tons
	16—100 tons		37—100 tons

cate that the conditions favorable to one of these fermentations are not always favorable to the other."

Every oxide and carbonate treatment, other than CaO, has largely augmented the 8-year losses of both sulfates and nitrates from the Cumberland

loam used by us. However, every addition of burnt lime ultimately gave large increase in leached nitrates although the heavier additions were initially inhibitory to both nitrification and sulfofication. Sulfofication was particularly inhibited in the subsoil with the 32-ton treatment and in the surface soil with the 100-ton treatment. The clay subsoil under the Cumberland loam was able to retain large quantities of sulfates regardless of variation in, or absence of treatment. With 8-ton treatments, this tendency was still marked after the first four years, and even after eight years it was evidenced for all treatments except MgO, being particularly noticeable in the case of the three native carbonates. Heavier additions of the more soluble forms, other than CaO, caused augmented occurrences of the alkali-earth elements and sulfates in the subsoil leachings, even before the end of the first four years. However, disparity between shallow- and deep-tank sulfate losses was still maintained by the heavier additions of the natural carbonates after eight years. The subsoil of the control, when unaltered by influx of added alkali-earth bases continued to manifest a decided ability to restrict the occurrence of sulfates in the leachings. This is amply demonstrated by the fact that the shallow control lost 534 pounds of SO_3 against only 24 pounds from the deep control over a six-year period. These losses represent 69 per cent of the rainfall sulfates in the former case and only 3.1 per cent in the latter. From similar unpublished findings upon a soil treated with soluble sulfate we have found that the leachability of added sulfate and engendered nitrates may be affected differently by treatment. Since this one-foot depth of clay, both subject to and devoid of influx of ameliorating bases added to the overlying soil, has continued to function as a barrier to the passage of sulfates over 8-year and 6-year periods, respectively, the effect and duration of such effect in the 3-foot depth of subsoil of the 5-year Cornell experiments appears problematical. Since our results show that the presence of calcium salts in the subsoil, as a result of leachings from the surface, exerts a marked effect upon the sulfate-retaining properties of the subsoil, it would appear that paucity or abundance of native calcium compounds would influence the action of the lower depths in changing the concentration of sulfates in the surface soil's leachings. Such changes in concentration of leachings have been exerted by the subsoil under the Cumberland loam in both directions, as determined by the treatment applied to the surface soil. Since the Dunkirk and Volusia subsoils vary decidedly in their calcium and carbonate content, it would seem plausible to assume that they would be at variance in their tendencies to alter the sulfate concentrations of the leachings from the surface soil. The points brought out serve to emphasize the value of parallel experimentation with shallow and deep tanks.

THIRTY-TWO-TON TREATMENT

Surface-soil tanks

With the exception of CaO, all of the 32-ton additions caused very decided increases in the leaching of sulfates during the initial year. Calcium oxide depressed the outgo very much below that of the control. The magnesium oxide and carbonate were responsible for the largest losses of sulfates. Next

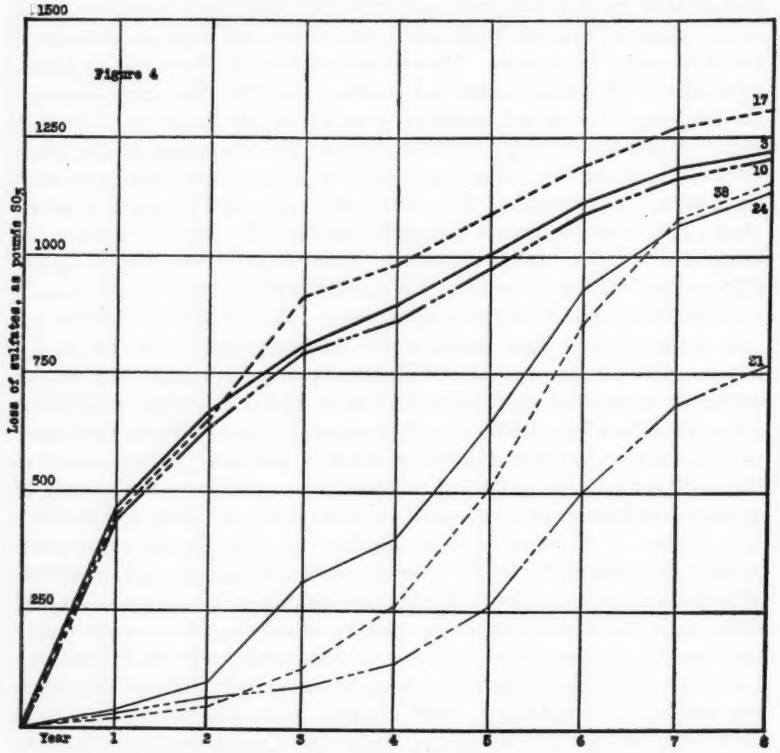

FIG. 4. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH $CaCO_3$ EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 3— 8 tons	Surface and subsoil	Tank 24— 8 tons
	10— 32 tons		31— 32 tons
	17—100 tons		38—100 tons

in order came the precipitated calcium carbonate while the three native carbonates were rather closely grouped in their influence.

During the second year the three native carbonates still exerted an activating influence approaching that of the other forms, exclusive of the burnt

TABLE 4

Sulfate content of leachings from loam soil with treatments equivalent to 32 tons CaO per acre

TANK NUMBER	TREATMENT	AS TO SUBSOIL	TOTAL VOLUME OF LEACHINGS	SO_3 LEACHED PER 2,000,000 POUNDS OF SOIL													
				1st year	2d year	3rd year	4th year	First 4-year period		5th year	6th year	7th year	8th year	Second 4-year period		Whole 8-year period	
								Annual average	Total					Annual average	Total	Annual average	Total
			liters	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
8	CaO	None	929	19	116	178	86	100	399	146	141	53	39	95	379	97	778
29	CaO	Clay	944	25	22	4	12	16	63	12	75	94	49	58	230	37	293
9	MgO	None	932	567	216	89	39	228	911	81	116	62	35	74	294	151	1205
30	MgO	Clay	968	18	489	361	97	241	965	78	152	83	32	86	345	164	1310
10	$CaCO_3$	None	1008	448	187	155	73	216	863	113	111	76	40	85	340	150	1203
31	$CaCO_3$	Clay	1024	29	30	24	50	33	133	128	240	185	84	159	637	96	770
11	$MgCO_3$	None	915	551	203	119	61	234	934	119	103	44	34	75	300	154	1234
32	$MgCO_3$	Clay	1034	55	594	430	138	304	1217	117	164	73	29	96	383	200	1600
12	Limestone	None	1082	399	172	123	65	190	759	114	112	73	42	85	341	138	1100
33	Limestone	Clay	1013	31	28	74	62	49	195	142	261	175	78	164	656	106	851
13	Dolomite	None	1026	403	238	197	80	230	918	158	153	125	74	138	510	179	1428
34	Dolomite	Clay	1038	39	78	225	98	110	440	178	278	188	98	186	742	148	1182
14	Magnesite	None	1077	426	176	118	82	201	802	116	107	111	35	92	369	146	1171
35	Magnesite	Clay	1086	21	45	269	138	118	473	227	300	150	66	186	743	152	1216
43	Wollastonite	Clay	1127	35	26	64	46	43	171	115	235	169	91	153	610	98	781
44	Serpentine	Clay	1207	42	19	7	14	21	82	6	38	33	26	26	103	23	185
Inches of rainfall				47.78	56.54	63.32	47.79	...	...	51.41	54.21	50.37	55.63	...	...	...	...

lime. During the third and fourth years, the yields were progressively and consistently decreasing. However, a reversion toward increase of sulfate outgo followed during the fifth and sixth years, after which came progressive depressions in the seventh and eighth years. In every case, both total and average annual results in the first half were larger than the corresponding amounts for the second half of the 8-year period. The totals for the 8 years were very nearly equivalent for the MgO, $CaCO_3$, $MgCO_3$, and magnesite, the limestone results coming next in order. The smallest outgo of sulfates for the full period came from the burnt lime, while the greatest came from the dolomite.

Soil-subsoil tanks

The amount of sulfates which passed from every treatment and through the subsoil was relatively meager during the first year and but a fraction of the amount which passed from the surface soil of corresponding treatment. Each treatment, however, caused a loss in excess of that from the deep control. It will be noted that there were no consistent increases during the second year from the treatments of $CaCO_3$, limestone, dolomite, and magnesite. However, a very striking increase was obtained from both MgO and $MgCO_3$. The limestone and $CaCO_3$ were still rather inactive during the third year, but both dolomite and magnesite had effected a material increase in the passage of sulfates. With the exception of precipitated $CaCO_3$, which still had failed to show any progressive increase in sulfate outgo, all treatments showed a smaller sulfate yield for the fourth year than for the third year. There was a general tendency toward progressive increases in outgo during the fifth and sixth years, followed by a progressive decrease through the seventh and eighth years. The average annual and the total losses from the deep tanks for the first 4-year period were greater than the corresponding figures from the shallow tanks in the case of the MgO and $MgCO_3$ treatments, while the reverse was true in the case of precipitated $CaCO_3$, limestone, dolomite and magnesite.

The results from tank 29, CaO treatment, are in decided contrast to those from the other tanks. The average annual outgo from this oxide was only 16 pounds for the first 4-year period, while that for the full 8-year period was only 37 pounds. The sulfate leachings from the corresponding surface-soil tank, No. 8, were also decidedly lower than those from the other treatments for both 4-year periods. The persistence of calcium hydrate in the soil of those tanks was established by a study of the speed of the reversion of the CaO to $CaCO_3$ which has been reported (6). The occurrence of $Ca(OH)_2$ in each leaching has been determined. The average hydroxide concentration for the several annual leachings are given in table 6. Those of the surface soil leachings were appreciable during the first three years, especially for the initial year. Though a decided drop occurred during the fourth year, the hydroxide persisted in the leachings through the fifth year. The persistence

of the calcium hydrate has been responsible for a marked depression in sulfate outgo for all years as compared with every other oxide or carbonate treatment and for the first year more especially in a comparison against the shallow con-

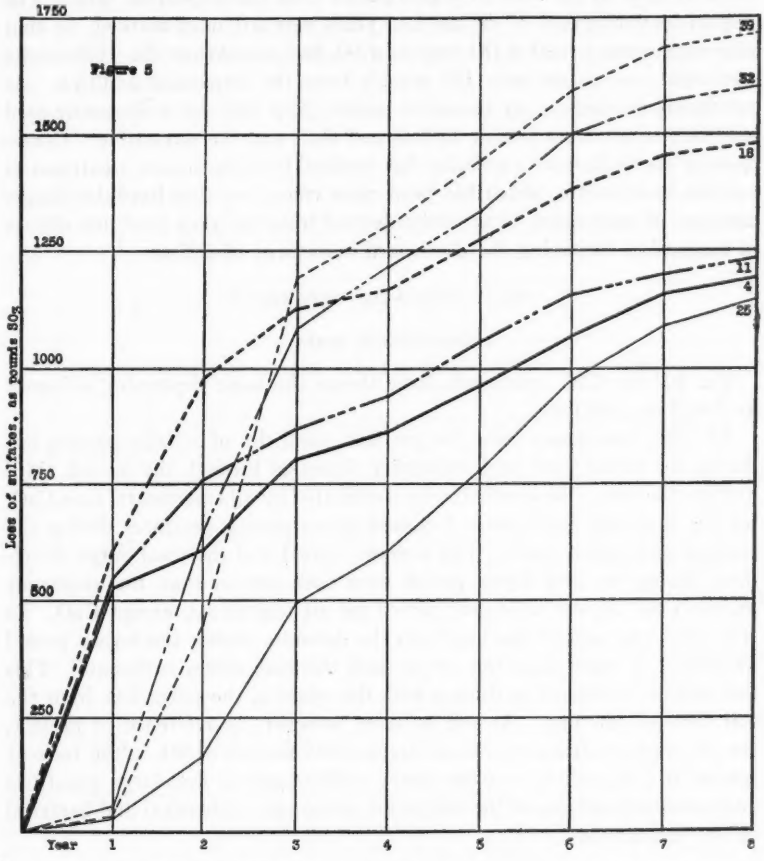

FIG. 5. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH $MgCO_3$ EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 4— 8 tons	Surface and subsoil	Tank 25— 8 tons
	11— 32 tons		32— 32 tons
	18—100 tons		39—100 tons

trol. Though not all-conclusive, this indicated depressed generation of sulfates in the surface soil. But, in spite of the ready solubility of $Ca(OH)_2$, the subsoil stopped its downward movement, and also that of the sulfates, which surface soil leachings indicated had passed into the subsoil.

Both wollastonite and serpentine increased the outgo of sulfates. However, after the initial year, a consistently larger yield came from the calcium silicate. The total of 171 pounds from this material during the first 4-year period was twice as large as the amount which passed from the serpentine tank. The disparities during each of the last four years were still more marked. so that after eight years a total of 781 pounds of SO_3 had passed from the wollastonite treatment, as against only 185 pounds from the serpentine addition. As previously pointed out by the senior author (5, p. 19), the wollastonite used was very much more readily hydrolyzed than was the serpentine. Consequently the wollastonite addition has resulted in a continuous treatment of calcium bicarbonate, which has been more efficacious than have the meager amounts of magnesium bicarbonate derived from the very insoluble silicate of magnesium in forcing the downward movement of sulfates.

ONE-HUNDRED-TON TREATMENT

Surface-soil tanks

The 100-ton CaO treatments have shown the same depressing influence as the 32-ton additions.

All other treatments show the greatest quantities of sulfates passing out during the initial year, with successive decreases through the second, third and fourth years. An upward trend is exhibited by all treatments, save CaO, for the fifth and sixth years, followed by successive decreases during the seventh and eighth years. The average annual and the total outgo of sulfates during the first 4-year period were both greater than the analogous amounts for the second 4-year period for all treatments, except CaO. In this series the sulfates leached from the dolomite during the 8-year period amounted to more than the outgo from the magnesium carbonate. This fact will be considered in dealing with the origin of the sulfur lost from the soil through leaching. As will be seen, however, by reference to table 1, the dolomite treatment carries an appreciable amount of SO_3 in the form of sphalerite (zinc sulfide) and the heavy addition means that large quantities and extensive surfaces of the sulfide are subjected to chemical and bacterial oxidative reactions.

Subsoil tanks

In the CaO tank of this series the average annual outgo of 16 pounds for the first 4-year period increased to an annual average of 127 pounds for the last four years. But the corresponding annual averages for the surface soil alone were only 22 pounds and 42 pounds. The 8-year total exceeded that of the shallow tank by 317 pounds. It may be that the leached lime either directly caused an increased formation of sulfates in the subsoil or a release by the subsoil of such sulfates as it may have held prior to the influx of calcium hydroxide and other calcium combinations. The MgO and $MgCO_3$ treat-

TABLE 5

Sulfate content of leachings from loam soil with treatments equivalent to 100 tons CaO per acre

TANK NUMBER	TREATMENT	AS TO SUBSOIL	TOTAL VOLUMES OF LEACHINGS	SO_3 LEACHED PER 2,000,000 POUNDS OF SOIL													
				1st year	2d year	3rd year	4th year	First 4-year period		5th year	6th year	7th year	8th year	Second 4-year period		Whole 8-year period	
								Annual average	Total					Annual average	Total	Annual average	Total
			liters	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
15	CaO	None	806	67	15	4	1	22	87	16	60	54	39	42	169	32	256
36	CaO	Clay	965	17	30	15	3	16	65	130	199	114	65	127	508	72	573
16	MgO	None	825	581	291	114	41	257	1027	88	102	61	19	68	270	162	1297
37	MgO	Clay	983	25	229	545	113	228	912	278	334	130	33	194	775	211	1687
17	$CaCO_3$	None	914	460	287	168	63	245	978	110	102	82	36	83	330	164	1308
38	$CaCO_3$	Clay	968	27	12	78	138	64	255	247	353	224	71	224	895	144	1150
18	$MgCO_3$	None	830	618	364	143	42	292	1167	109	110	64	32	79	315	185	1482
39	$MgCO_3$	Clay	928	38	410	742	113	326	1303	138	154	87	31	103	410	214	1713
19	Limestone	None	972	402	215	139	64	205	820	119	106	70	36	83	331	144	1151
40	Limestone	Clay	1069	40	87	60	48	59	235	150	316	227	91	196	784	127	1019
20	Dolomite	None	906	417	325	279	130	288	1151	286	300	237	119	236	942	262	2093
41	Dolomite	Clay	1006	27	18	89	34	42	168	315	560	385	199	365	1459	203	1627
21	Magnesite	None	987	509	181	160	70	230	920	116	128	88	44	94	376	162	1296
42	Magnesite	Clay	1054	22	22	138	95	69	277	226	399	246	88	240	959	155	1236
Inches of rainfall				47.78	56.54	63.32	47.79	...	...	51.41	54.21	50.37	55.63	...	.....	...	...

ments both increased the sulfate outgo during the second year with still further increases during the third year after which there was a drop. For the first 4-year period almost as much sulfate was lost through the subsoil as from the surface soil, while for the $MgCO_3$ additions the outgo was actually greater. The precipitated $CaCO_3$ and natural carbonates, however, caused a decidedly smaller loss of total sulfates from soil plus subsoil than from the surface soil alone. The amount of SO_3 lost from every subsoil tank during the second 4-year period was decidedly larger than that of the corresponding shallow tank. The fifth and sixth years' losses from the MgO and $MgCO_3$ tanks were greater than those of the fourth year. This increase was followed by a progressive decrease during the seventh and eighth years. The 8-year losses from those two materials were also greater when the leachings passed through the subsoil. The excess losses of 380 and 231 pounds of SO_3 from subsoil tanks treated with MgO and $MgCO_3$ demonstrate that the leached sulfates were derived in part from the subsoil. This does not obtain, however, in the case of the three natural carbonates and in the case of precipitated $CaCO_3$.

EFFECT OF FORM AND RATE OF TREATMENT ON LOSS OF SULFATES

The effect of rate of treatment is shown in the graphs, figures 1 to 8.

Burnt lime

Previously reported (6) residual carbonate analyses showed that the hydrate of the 8-ton CaO application had practically all passed from that form after a few weeks. But the direct CaO absorption and carbonation reactions continued for a much longer period where the hydrate persisted from the two excessive rates of 32 and 100 tons. This difference in the persistence of calcium hydrate is reflected in the larger sulfate outgo of the 8-ton treatment and the smaller loss from each of two heavier treatments, especially in the case of the surface soil for the first three years. The lesser handicap imposed upon the soil treated at the 8-ton rate during the period required for reversion of $Ca(OH)_2$ to $CaCO_3$ was, however, apparently overcome and followed by accelerated sulfofication. As a result totals for both the initial 4-year period and the full 8-year period approached the corresponding totals from calcium carbonate for both depths. Yet, the persistence of the $Ca(OH)_2$ in the two heavier treatments continued to depress the outgo so that the total for the 8-year period in the 32-ton treatment amounted to only 778 pounds, or an annual average of 97 pounds, while a still smaller total of 256 pounds, or an annual average of 32 pounds, came from the 100-ton treatment. If decreased outgo and depressed sulfate generation be identical, it would appear that the excessive amounts of lime partially inhibited sulfofication. As an alternative, however, it might be assumed that the burnt lime had not depressed sulfofication and that such had continued normally, or even with acceleration, in the more open and better aerated soils containing the heavier

treatments in particular. It would follow, then, that such engendered sulfates were less soluble in the $Ca(OH)_2$-impregnated water, and hence were not washed out in the leachings. This alternative finds support from two angles. First, the rainfall which passed through heavy CaO additions often contained less sulfates as leachings than it did as rain water. Secondly, the

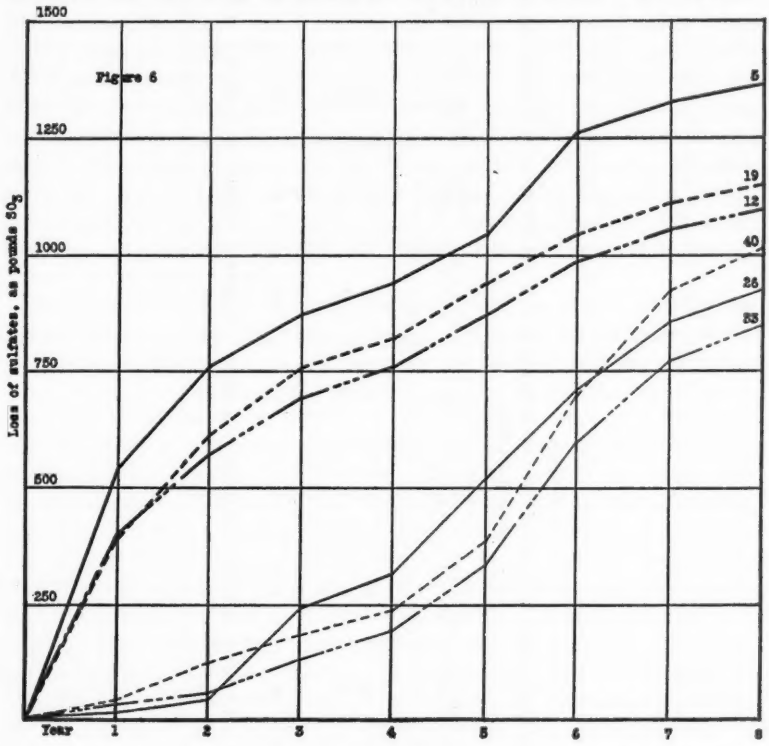

FIG. 6. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH LIMESTONE EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 5— 8 tons	Surface and subsoil	Tank 26— 8 tons
	12— 32 tons		33— 32 tons
	19—100 tons		40—100 tons

initial inhibition of the parallel biochemical process of nitrification was followed by intensive acceleration after the first annual period.

Solubility of calcium sulfate in lime water

In searching for data upon the solubility of $CaSO_4$ in solutions of $Ca(OH)_2$, we have found only the data of Cameron and Bell (1), given also by Seidell

TABLE 6

Average normality of $Ca(OH)_2$ in each annual leaching from tanks treated with CaO at the rate of 8, 32 and 100 tons as determined from the analysis of each periodic leaching

RATE OF ADDITION	AS TO SUBSOIL	FIRST YEAR 1914–15	SECOND YEAR 1915–16	THIRD YEAR 1916–17	FOURTH YEAR 1917–18	AVERAGE FIRST 4 YEARS 1914–18	FIFTH YEAR 1918–19	SIXTH YEAR 1919–20	SEVENTH YEAR 1920–21	EIGHTH YEAR 1921–22	AVERAGE SECOND 4 YEARS 1918–22	AVERAGE FOR 8-YEAR PERIOD 1914–22
tons												
8	None	0	0	0	0	0	0	0	0	0	0	0
8	Clay	0	0	0	0	0	0	0	0	0	0	0
32	None	0.00789	0.00136	0.00162	0.00035	0.00281	0.0004	0	0	0	0.00010	0.00161
32	Clay	0	0	0	0	0	0	0	0	0	0	0
100	None	0.02023	0.02113	0.01937	0.00657	0.01683	0.00654	0.00300	0.00183	0.00115	0.00313	0.00998
100	Clay	0	0	0	0	0	0	0	0	0	0	0

(10). These investigators subjected aqueous and lime water suspensions of gypsum to constant agitation at 25°C. for two weeks and determined the concentration of $CaSO_4$. They used eleven aqueous solutions of $Ca(OH)_2$ containing 0.062–1.166 gm. CaO per liter. With increase in concentration of $Ca(OH)_2$ there occurred a decrease in amount of $CaSO_4$ in solution. However, the minimum concentration of $CaSO_4$ given by Cameron and Bell was much greater than that of the maximum concentration found in the tank leachings. Calculating SO_3 losses to equivalence of $CaSO_4$ the maximum concentration possible in our leachings was 0.1884 gm. per liter. But this concentration is the $CaSO_4$ equivalent of the 0.3231-gm. $BaSO_4$ determination upon the composite which gave the maximum annual loss of 742 pounds of SO_3 from the 100-ton $MgCO_3$ treatment. Furthermore, the cited data were obtained from gypsum, rather than from freshly precipitated $CaSO_4 \cdot 2H_2O$, such as would be found in the soil. We have, therefore, sought additional data, particularly with reference to the freshly precipitated hydrated material.

Before considering such data, however, it would be well to consider the concentrations of $Ca(OH)_2$ in the drainage waters of the six tanks which received applications of CaO. These concentrations for each annual period were derived by averaging the hydroxide titration values of the several periodic leachings and are given in table 6. No $Ca(OH)_2$ passed from the 8-ton additions made to either shallow or deep tanks. The presence of hydroxide was established for each of the first five years in the case of the surface soil leachings from the 32-ton additions, the maximum occurring during the first annual period, with a decided drop for the second and third years and with still further decreases, progressively for the fourth and fifth years. No $Ca(OH)_2$ ever appeared in the leachings which passed through the subsoil in the tank receiving CaO at this rate. The initial concentration and that maintained through the first three years were very much higher for the surface-soil leachings from the 100-ton additions than for the 32-ton treatment. Some $Ca(OH)_2$, derived in the main from the 100-ton treatment residues in the lower zones of surface soil, has persisted intermittently throughout the 8-year period. Again, however, as in the 32-ton additions, no calcium hydroxide has passed through the 1-foot zone of clay subsoil.

With these figures before us, we may better consider the solubility of $CaSO_4 \cdot 2H_2O$ as given in table 7 and apply such data as explanatory of the sulfate losses induced by CaO additions as given in tables 3, 4 and 5. Analysis A reported in table 7 was made in 1920 upon an aged concentrate standing over a large quantity of solid-phase $Ca(OH)_2$. Analysis B was made in 1923 upon the same solution again brought to saturation after the addition of water. The normality values found in both analyses for saturation at 25°C. were higher than those given by Seidell (10). The initial and final titration values of the $Ca(OH)_2$ solutions, varying only within analytical error, show that no $Ca(OH)_2$ was changed from the solution phase to the solid

phase by contact with the excess of solid-phase calcium sulfate. The table shows that the highest $Ca(OH)_2$ concentrations in the 100-ton-treatment leachings, 0.02113 normal, somewhat less than one-half saturation, could carry at least 1.75 gm. of calcium sulfate per liter. This amount is more than 9 times that of the heaviest $CaSO_4$ content found in the annual leachings. Contact of engendered sulfates and soil water impregnated with $Ca(OH)_2$ could hardly be such as to insure saturation of the solid in the solvent. The ratio of more than 9 to 1 would serve, however, as an offset to the lesser opportunity of the soil water to effect concentration of sulfates, were such widely diffused throughout the soil. We have other unpublished data relative to the influence of lime upon the outgo of applied sulfates from another soil. These data establish the tendency of the lime-treated soil to retard

TABLE 7

The solubility of anhydrous and freshly precipitated calcium sulfate in solutions of calcium hydroxide at 25°C.

ANALYSIS A, 1920—AGITATION INTERMITTENTLY FOR 3 HOURS AND 16 HOURS CONTACT—5.0 GM. CHARGES PER 500 CC. OF WATER		ANALYSIS B, 1923—72 HOURS CONTACT WITH FREQUENT AGITATION—20 GM. CHARGES PER 500 CC. OF WATER					
		Anhydrous calcium sulfate*			Freshly precipitated $CaSO_4 \cdot 2H_2O$		
Anhydrous calcium sulfate*		Normality of $Ca(OH)_2$		$CaSO_4$ dissolved per liter of $Ca(OH)_2$	Normality of $Ca(OH)_2$		$CaSO_4$ dissolved per liter of $Ca(OH)_2$
Normality of $Ca(OH)_2$	$CaSO_4$ dissolved per liter of $Ca(OH)_2$	Before contact with $CaSO_4 \cdot 2H_2O$	After contact with $CaSO_4 \cdot 2H_2O$		Before contact with $CaSO_4 \cdot 2H_2O$	After contact with $CaSO_4 \cdot 2H_2O$	
	gm.			*gm.*			*gm.*
0	1.9160	0	0	2.1695	0	0	2.0464
0.0047	1.8600	0.00440	0.00430	1.8633	0.00448	0.00440	1.9630
0.0119	1.7740	0.01120	0.01090	1.9240	0.01121	0.01101	1.8996
0.0238	1.6560	0.02240	0.02190	1.7980	0.02240	0.02201	1.7694
0.0475	1.5620	0.04480	0.04480	1.7303	0.04480	0.04480	1.7607

* From J. W. Owen & Co., Philadelphia.

the outgo of added sulfates during the persistence of $Ca(OH)_2$. If sulfates had accumulated in excessive amounts during the persistence of $Ca(OH)_2$ in the the Cumberland loam, it would be expected that the rapid removal of sulfates would follow the disappearance of the hydroxide. But instead of such a marked transition in rate of sulfate outgo, there has occurred a gradual increase in sulfate emissions, as though the soil flora were slowly regaining their vigor and ability to manufacture sulfates, after the continued excessive causticity and during the maintenance of a materially lessened, though still positive, alkalinity.

These data, as a whole, do not prove that the relative decrease in sulfate outgo caused by the heavier treatments was due entirely to initial biological inhibition, nor do they establish the fact that the heavy treatments main-

tained such an inhibition. But they do establish the fact that there was in the early stages an inhibitory influence of some kind. The initial inhibition disappeared in time as a result of the carbonation of the excess of $Ca(OH)_2$. This chemical transition was the dominant causative factor controlling initial inhibition and later acceleration, whether the effect be considered the result of biochemical, physical or chemical changes in the soil, or a combination of the three.

Magnesium oxide

The effect of MgO, however, was different from that of CaO. As indicated by the composition of the leachings, the quantity of $MgCO_3$ formed from the oxide of magnesium was such as to constitute a treatment of $MgCO_3$. This carbonate, both applied and oxide-derived, was more rapidly and intensively fixed by the soil and at the same time the unabsorbed excess was more quickly and intensively leached. Furthermore, any hydrated MgO derived from the MgO additions was very much less soluble than the hydrate of calcium. Consequently, there was no problem as to repressed solubility of soil-engendered magnesium sulfate. The heavy sulfate leachings from the MgO additions indicated that the low concentration of $Mg(OH)_2$ in the soil water did not inhibit nor depress sulfofication. It will be noted that the sulfate losses of the initial year, those of the first 4-year period, and those of the full 8-year period increased in the order of increasing rates of treatment. Thus, the surface soil tanks treated at the rates of 8, 32 and 100 tons lost 1118, 1205, and 1297 pounds, respectively.

In the case of the subsoil tanks the peak of the sulfate outgo came during the third year for both 8-ton and 100-ton MgO additions. But in the case of the 32-ton treatment the greatest losses occurred during the second year. This finding evidently involves some system balance, for the presence of magnesium bicarbonate in the leachings was observed to have occurred in the same manner. Furthermore, the $MgCO_3$ additions behaved in the same way, with reference both to sulfates and bicarbonate of magnesium. That is, the subsoil drainages from the magnesium oxide and carbonate tanks were for a time low in both their sulfate and magnesium bicarbonate contents, and then with the advent of increased concentration of one substance there occurred a parallel increase in that of the other.

Calcium carbonate

During the third year which was one of abnormal rainfall the 8-ton deep tank lost three times the amount lost during the first two years. A drop during the fourth year was followed by increases during the fifth and sixth years, after which occurred progressive decreases during the seventh and eighth years. But in the case of the 32-ton addition in the deep tank, the small amounts of the first four years were succeeded by increased losses during the fifth, sixth, and seventh years, with a decrease in the eighth year. Where

the $CaCO_3$ additions to the deep tank were at the 100-ton rate, the small losses of the first three years were followed by maintained increases during the fourth, and more particularly the fifth, sixth and seventh years, after which occurred a decided drop. Accordingly, the 8-year total SO_3 losses from the 32-ton treatment amounted to but 770 pounds, as contrasted with corresponding totals of 1133 pounds and 1150 pounds for the 8-ton and 100-ton treatments, respectively. Likewise, the first 4-year period total from the 32-ton addition was less than that of either the 8- or 100-ton addition. It would seem that the 32-ton treatment would be sufficiently extensive to give a thoroughly disseminated treatment throughout the mass of soil, so that the soil-water would become saturated with calcium bicarbonate. Both 32- and 100-ton additions should afford directly dissolved calcium in amounts greater than the amount dissolved from the 8-ton treatment. Thus, if calcium carbonate, or bicarbonate were to be considered as depressive, both 32- and 100-ton treatments would be expected to yield smaller quantities of sulfates than those coming from the 8-ton treatment. But during each 4-year period the sulfate outgo from the 32-ton treatment lagged behind the losses from both the 8- and 100-ton additions. As the converse of the magnesium additions, where both magnesium bicarbonates and sulfates appeared first and for a time most extensively in the leachings from the 32-ton addition of magnesium oxide and carbonate, unpublished data from these tanks show that the 8- and 100-ton $CaCO_3$ treatments both yielded more $CaCO_3$ than did the 32-ton treatment during the first and second 4-year periods, and of course, greater also for the full 8-year period. As in the case of the $MgCO_3$ converse, at the same equivalent rate, a system balance would also seem to be of effect in the 32-ton $CaCO_3$ treatment.

Magnesium carbonate

The total amount of sulfates from the magnesium carbonate additions have increased slightly with each increase of treatment. The 8-, 32- and 100-ton treatments have caused leaching totals of 1189, 1234, and 1482 pounds, respectively, from the surface soil. In each case, the maximum outgo has occurred during the initial year, with the next largest outgo during the second year and the third largest during the third year. After the third year the amounts passing from the residual sulfur reserves are comparatively small. In this connection it should be pointed out that a number of the annual sulfate leachings from this treatment are actually less than the amounts found to have been brought down by rain water. This observation is common to a number of the other treatments. It is rather interesting to note that, particularly in the case of the subsoil tanks, a treatment may so retard the passage of sulfates as to cause the sulfate concentration of the leachings to be lower than that of rainfall, before the treatment begins to push itself and the sulfate of its basic ion through the subsoil, and that the same partial accumulation of the rainfall sulfates may be evidenced after the maxima sulfate yields have passed.

Limestone-dolomite-magnesite

The three native carbonates acted in a similar manner at each rate, by inducing the largest losses of sulfates from the surface soil during the initial year with consistent, progressive decreases during the following three years. Each of the three natural products also caused an upward trend in the outgo curve, with practically identical amounts during the fifth and sixth years, followed by a downward trend during the seventh and eighth years. The first 4-year-period yield and the total outgo from the limestone, dolomite, and magnesite were rather close for the 8-ton additions. The sulfate outgo, however, from the 32- and 100-ton additions drew away from the losses shown by the 8-ton treatment during the first 4 years with a still further disparity during the second half of the 8-year period. It would appear that the sulfide impurity of the dolomite had served as a source for increased sulfate generation particularly after the fourth year.

Where the three natural materials were applied to the deep tanks at the 8-ton rate, the totals for the first 4-year period were less in each case than the respective initial year losses from the surface soil alone. The largest subsoil outgo of the first 4-year period came during the third year in each case. During the fifth year there was a marked increase in the sulfate outgo from each material, the largest outgo for the second period coming, however, in the sixth year, after which there was a progressive downward tendency for the last two years.

In the case of the 32-ton applications, the largest annual loss of the first 4-year period also occurred in the third year. During the fifth, sixth and seventh years, all three materials gave decided increases over corresponding losses of the fourth year, followed by a very decided decrease for each addition during the eighth annual period.

There were no greatly accelerated movements of sulfates through the subsoil from either of the three natural products at the 100-ton rate for any one of the first four years, with the possible exception of magnesite during the third year. During the first three years of the second 4-year period, however, the amounts of sulfates leached through the subsoil were materially augmented particularly in the case of the dolomite, the yield from which was in excess of that from any one of the shallow tanks. This indicates either the passage of the sphalerite-derived sulfates from the dolomite treatment in the surface soil or else an activated sulfate generation or sulfate liberation in the subsoil as induced by the specific ratio of calcium-magnesium salts supplied by the dolomitic limestone.

RELATION OF TOTAL SULFATE LOSSES TO SOURCES OF SULFUR

The shallow tanks have three sources from which the leached sulfates may have been drawn—soil, treatment, and rainfall. The deep tanks have the subsoil as an additional source. Although the SO_3 content of the subsoil

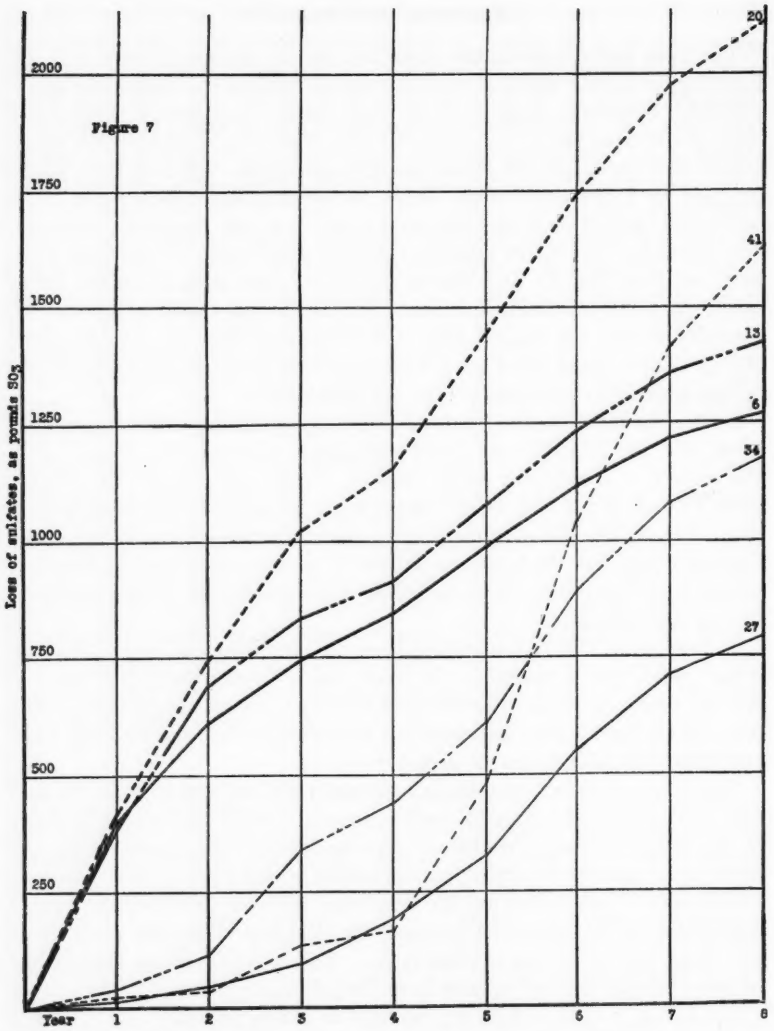

FIG. 7. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH DOLOMITE EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 6— 8 tons	Surface and subsoil	Tank 27— 8 tons
	13— 32 tons		34— 32 tons
	20—100 tons		41—100 tons

was found to be less than that of the surface soil, there was more SO_3 supplied by the clay than by the soil, because of the 1-foot depth of the subsoil, as against 8 inches of surface soil. In considering the relationship of outgo to the amounts of sulfur added in treatments, we have to deal only with MgO, $MgCO_3$, $CaCO_3$, dolomite, and magnesite, since the limestone and burnt lime were sulfur-free.

It is of course difficult, if not impossible, to determine definitely the source of the sulfates found in the leachings; yet, certain proportionate relationships may be established. For instance, in some cases the annual sulfate outgo was less, and in others decidedly more, than the amount of SO_3 washed down by the rainfall. In other instances the amounts of sulfates in the leachings which passed through the subsoil were greater than the amounts leached from the surface soil alone, demonstrating the fact that a fraction of the outgo was necessarily derived from the subsoil. Such relationships for the 8-year period are given in table 8.

Eight-ton treatment

Since each treated shallow tank gave a sulfate outgo greater than that of the rainfall, it must be assumed that some of the leached sulfates were derived from either treatment or soil, or both. The sulfate total carried from the soil and through the subsoil was greater than that brought down by rainfall in the case of each of the three additions, MgO and precipitated carbonates of calcium and magnesium, but it was less for the burnt lime, limestone, dolomite, and magnesite. However, if all rainfall sulfates were leached through the surface soil, the 7 treatments show an average per acre loss of only 167 pounds of SO_3 to be charged jointly against soil and treatment impurities. Assuming no sulfur additions to the surface soil from treatment or rainfall during the 8-year period, all of the seven treatments at this rate caused losses in excess of one-half of the store present in the soil at the beginning of the experiment. When considered as the proportionate part of the sulfur carried by both soil and subsoil, each sulfate outgo from the deep tank is less than one-fifth of that possible from these two sources. The 6-year-period outgo of sulfur from the shallow control was less than the sulfate content of rainfall and only 25.2 per cent of the amount originally present in the soil. The outgo from the subsoil control was but one-twenty-second of that from the shallow control and only 0.5 per cent of the total native sulfur content of soil and subsoil.

The yield of sulfates in the leachings over the 8-year period was many times the amount added through the impurities of the treatment, for all of those additions, save dolomite, where the proportions were only 1.81 to 1 for the shallow tank and 1.13 to 1 for the deep tank.

When the sulfate losses from the surface soil are expressed as per cent of the total sulfur supplied from all sources, all treatments show a loss of one-third or more of that possible. A maximum of 19.3 per cent and a minimum

TABLE 8

Relation of total SO_3 leached to total available in soil, treatments and rainfall for the whole 8-year period

TREATMENT	SO_3 CARRIED IN LEACHINGS									
	From surface soil only					From surface soil and subsoil				
	Total amount per 2,000,000 lbs. of soil	As per cent of the sulfur content of soil	As multiple of SO_3 added in treatment	As per cent of SO_3 in rainfall	As per cent of total available from all sources	Total amount per 2,000,000 lbs. of soil	As per cent of the sulfur in soil and subsoil	As multiple of SO_3 added in treatment	As per cent of SO_3 in rainfall	As per cent of total available from all sources
	lbs.	*per cent*		*per cent*	*per cent*	*lbs.*	*per cent*		*per cent*	*per cent*
8-ton rate										
CaO	1104	52.1	.....	107.3	35.1	992	20.3	.....	96.4	16.8
MgO	1118	52.7	37.26×	108.6	35.2	1150	23.5	38.33×	111.7	19.3
$CaCO_3$	1222	57.6	16.97×	118.7	37.9	1133	23.1	15.73×	110.1	18.9
$MgCO_3$	1189	56.1	32.13×	115.5	37.3	1146	23.4	30.97×	111.3	19.3
Limestone	1261	59.5	.....	112.8	40.0	931	19.2	.....	90.5	15.7
Dolomite	1271	60.0	1.81×	123.4	33.0	793	16.2	1.13×	77.1	12.0
Magnesite	1206	56.9	36.50×	117.2	37.9	815	16.7	24.70×	79.2	13.7
32-ton rate										
CaO	778	36.7	.....	75.6	24.7	293	6.0	.....	28.5	4.9
MgO	1205	56.8	10.04×	117.1	36.9	1310	26.8	10.29×	127.3	21.7
$CaCO_3$	1203	56.7	4.18×	116.8	35.0	770	15.7	2.67×	74.8	12.4
$MgCO_3$	1234	58.2	8.34×	119.9	37.4	1600	32.7	10.81×	155.5	26.4
Limestone	1100	51.9	.....	106.9	34.9	851	17.4	.....	82.7	14.4
Dolomite	1428	67.4	0.51×	138.8	24.0	1182	24.2	0.42×	114.9	13.5
Magnesite	1171	55.2	8.87×	113.8	35.7	1216	24.9	9.21×	118.2	20.1

100-ton rate										
CaO	257	12.1	.....	24.9	8.2	573	11.7	.....	55.7	9.7
MgO	1297	61.1	3.46×	126.0	36.8	1687	34.5	4.50×	163.9	26.8
$CaCO_3$	1308	61.7	1.45×	127.1	32.3	1150	23.5	1.28×	111.7	16.9
$MgCO_3$	1482	69.9	3.20×	144.0	41.0	1713	35.0	3.70×	166.5	26.8
Limestone	1151	54.3	.....	111.9	36.6	1019	20.8	.....	99.0	17.2
Dolomite	2093	98.9	0.24×	203.7	17.6	1627	33.3	0.19×	158.1	11.1
Magnesite	1296	61.1	3.14×	125.9	36.4	1236	25.3	2.99×	120.1	19.5
32 tons of material applied										
Wollastonite	....	....	.....	.....	....	781	16.0	19.53×	75.8	13.1
Serpentine	....	....	.....	.....	....	185	3.8	1.03×	18.0	3.0
Control—no treatment										
None	534*	25.2	.....	69.0	18.5	24*	0.5	.....	3.1	0.4

* Six years.

of 12.0 per cent of that available from all sources, including the subsoil, were found to have passed through the treated soil-subsoil tanks. In the controls, only 18.5 per cent of that possible from the surface-soil control and but 0.4 per cent of that possible from the deep-tank control were found in the total leachings after 6 years.

Thirty-two ton treatment

Either partial sterilization, increase in the soil's retentive properties, depressed solvent action, desulfofication, or a combination of these factors resultant from this CaO treatment was responsible for a sulfate outgo of but 36.7 per cent of the amount originally present in the surface soil, and only 6.0 per cent of that contained originally by both soil and subsoil. In each of the other oxide and carbonate treatments in the shallow tanks, the leached SO_3 amounted to more than 55 per cent of that native to the soil. The several magnesic materials caused the deep tanks to lose from one-fourth to one-third of the sulfur originally present in the soil plus subsoil. As previously noted, the smaller outgo from the 32-ton $CaCO_3$ treatment held not only for sulfates, but also for calcium; i.e., a smaller total of both sulfates and calcium passed through the subsoil from 32-ton equivalent than from either the 8-ton or the 100-ton equivalent. Expressed as per cent of the total sulfates supplied to the surface soil from all sources, the MgO, $CaCO_3$, $MgCO_3$, limestone, and magnesite each had induced a sulfate outgo equivalent to slightly more than one-third of that possible; while the CaO and dolomite were responsible for losses of smaller proportions. Based on amounts from all sources, including the subsoil, the deep-tank losses varied from a minimum of 4.9 per cent, in the case of CaO, to a maximum of 26.4 per cent, in the case of $MgCO_3$.

Both wollastonite and sepentine failed to push through an amount of sulfate equivalent to that of the rainfall. The SO_3 leached from the serpentine tank was only 18 per cent of that which was brought to it by rainfall. The wollastonite and serpentine yielded 13.1 per cent and 3.0 per cent, respectively, as the fractions of sulfur available from all sources.

One-hundred-ton treatment

The sterilizing activities and other factors mentioned in the discussion of the 32-ton results were of still greater effect in the 100-ton addition, which was responsible for losses approximately one-eight of the total sulfur in the surface soil. Since the amount of sulfates which passed through the deep tank which contained CaO was more than twice as great as the amount which was lost from the corresponding shallow tank, it is evident that the larger fraction of the sulfate outgo was derived from the subsoil. The heavy CaO treatments so depressed the surface-soil sulfate outgo that the amount leached represented only one-fourth of the amount brought down in the rain water. The sulfates derived from the subsoil increased the sulfate yield to 55.7 per cent of the

sulfur brought down in the rain water. The sulfate leachings from the heavy CaO additions were depressed to 8.2 per cent and 9.7 per cent of the amounts derived from all sources, for the surface soil and the soil-subsoil, respectively.

Calculated to 8-year totals, with the exception of CaO, the sulfate outgo from each surface soil tank treated at the 100-ton rate was in excess of the amount carried by the rain water. The same was true for the deep tanks,

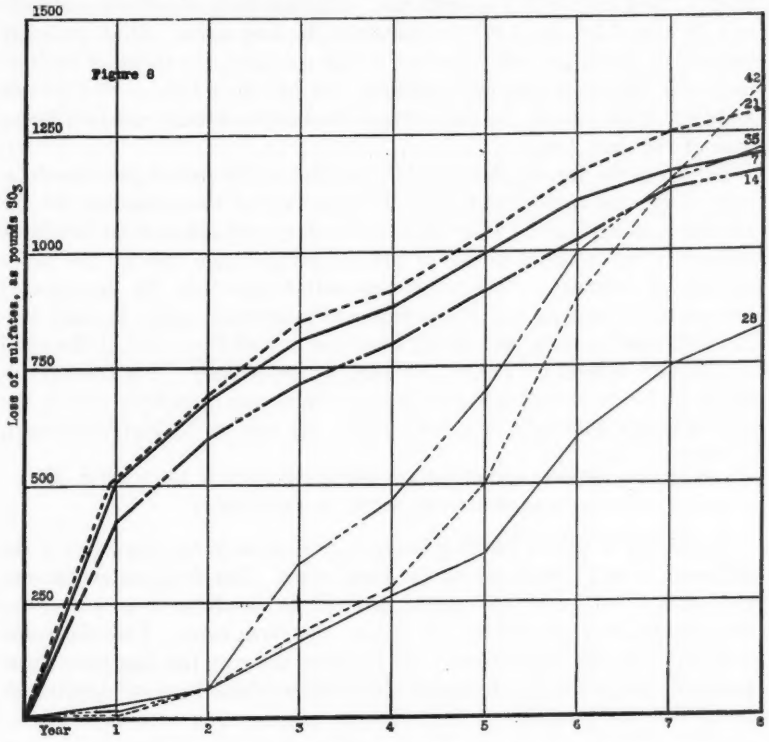

FIG. 8. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH MAGNESITE EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 7— 8 tons	Surface and subsoil	Tank 28— 8 tons
	14— 32 tons		35— 32 tons
	21—100 tons		42—100 tons

with the added exception of the limestone treatment, and this exception amounted to 99.0 per cent of the rain water content. The heavy losses from the dolomite shallow tank represented an amount equivalent to 203.7 per cent of the rainfall sulfur.

Expressed in relationship to the amount of SO_3 found in the surface soil, the seven treatments other than CaO caused sulfate leachings of 54.3–98.9

per cent of the amount originally contained in the surface soil. These same six treatments gave sulfate losses ranging from the limestone minimum of 20.8 per cent to the $MgCO_3$ maximum of 35.0 per cent of that possible where the leachings passed through both soil and subsoil.

The amounts of sulfates leached from the surface soil were 3.46, 1.45, 3.20, and 3.14 times the sulfur impurities of the treatments for MgO, $CaCO_3$, $MgCO_3$, and magnesite, respectively. Corresponding respective multiples of 4.50, 1.28, 3.70, and 2.99 were found for the deep tanks. Most probably because of the larger sulfur content of the dolomite, the outgo of sulfates from this treatment was approximately one-fourth of that carried by the addition, in the case of the shallow tank, and approximately one-fifth in the case of the deep tank.

In spite of the magnitude of the SO_3 leachings which passed from the dolomite, they were equivalent to only 17.6 per cent of that available for the shallow tank and but 11.1 per cent for the deep tank, because of the large amount of sulfur added to that of soil and precipitation through the sulfur content of treatment. The other two native materials, the precipitated carbonates of calcium and magnesium and magnesium oxide, induced surface-soil losses ranging between 32.3 per cent and 41.0 per cent of the total of all sulfur sources for $CaCO_3$ and $MgCO_3$, respectively. The corresponding range for the subsoil tanks was from the minimum of 16.9 per cent in the case of $CaCO_3$ additions, to 26.8 per cent in the case of the MgO treatment.

RELATION OF 8-YEAR TOTALS OF OUTGO TO SOURCE OF SULFUR, AS INFLUENCED BY RATE OF TREATMENT

Periodicity of sulfate leaching has been considered in the discussion of the influence of each treatment at the three rates. The divergences between the initial activity and that exerted through the remaining seven years have been shown for each addition at each of the three rates. This discussion will deal with the proportional relationships between the aggregate losses for the 8-year period and the amounts of sulfur available from soil, treatment-impurities, and rainfall.

Burnt lime

Since the outgo of sulfates from the surface soil decreases with increase in treatment, with constant initial soil content and precipitation, and with no sulfur added by the oxide, it follows that the percentage relationship of outgo also decreases with increased rates of application. There is a corresponding per cent decrease when the diminishing surface-soil losses are calculated as fractions of the constant total of all sources of sulfur. The total sulfate outgo from the deep 8-ton tank is almost equivalent to that from the surface soil alone; hence the per cent loss drops from 52.1 to 20.3 of the combined sulfur stores of soil and subsoil. With a distinct decrease in the SO_3 leachings through the subsoil from the 32-ton addition, and the addi-

tional sulfur content of the subsoil, the per cent of the possible drops to the low figure of 6.0. But in the case of the 100-ton addition, the burnt lime has either carried through more of the rain water sulfates or forced the liberation of sulfates already held as such, or else it caused the generation and liberation of additional sulfates from the subsoil. Hence, the augmented amount represents 11.7 per cent of the original sulfur content of soil plus subsoil.

Expressed as fractions of the sulfur content of rain water collections, the SO_3 losses from surface soil show a progressive decrease in per cent—107.3, 75.6, and 24.9, respectively, for the 8- 32- and 100-ton additions. The SO_3 forced through the subsoil by the 8-ton addition represents the nearest approach to the amount of sulfur brought down by rainfall. That which passed from the 100-ton subsoil tank amounted to a little more than one-half of the amount derived from rainfall. A still smaller amount, about one-fourth of that of the rain water, came through from the soil-subsoil tank which received burnt lime at the 32-ton rate.

Magnesium oxide

The MgO additions of 8, 32 and 100 tons were responsible, respectively, for sulfate leachings equivalent to 52.7, 56.8 and 61.1 per cent of the soil's initial sulfur content. With no great variation in amounts of sulfur lost from the surface soil, treated at the three rates, and with increasing amounts carried as impurities, the factors for outgo-to-treatment relationship decreased with increasing treatments. With uniformity in sulfate losses from the surface soil for the three rates and the approximation in amounts of sulfur available from all sources for each rate, there followed a uniform relationship of outgo-to-source, approximately 36 per cent.

The sulfate losses of 1150, 1310, and 1685 pounds from the deep tanks treated at the rates of 8, 32, and 100 tons, amounted to 23.5, 26.8, and 34.5 per cent, respectively, of the initial sulfur content of soil plus subsoil. Likewise, the increasing proportions of outgo to the totals available from all sources, 19.3, 21.7, and 26.8 per cent, were induced, respectively, by the 8-, 32- and 100-ton treatments. The factors of outgo-to-impurities for the deep tanks decreased with increasing rates of treatment—38.33, 10.92, and 4.50 for 8, 32 and 100 tons, respectively.

Each MgO addition caused the surface soil to yield sulfates in excess of the amount carried by rainfall, the per cent relationships increasing with intensity of treatment. The same as to excess of leachings over rainfall content and order of per cent relationships held true for the deep tanks. Each deep-tank total, however, was greater than that of the corresponding shallow tank, establishing the fact that MgO effected a derivation of sulfates from both soil and subsoil.

Calcium carbonate

Each of three shallow tanks gave a sulfate outgo close to 60 per cent of the original sulfur content of the soil. The sulfate losses from the 8-, and 32-ton additions were closely approximate, and somewhat less than the outgo from the 100-ton-equivalent addition. The outgo-to-total-source relationship and the impurity factors decreased with increase of treatment. Since the sulfate losses did not increase consistently with increase in treatment, the relation between outgo and rainfall sulfates also failed to show per cent increase with increased applications.

The sulfate leachings from the deep tanks approached those from the shallow tanks for the 8-ton and 100-ton additions but were decidedly less for the 32-ton treatment. As stated this relationship holds not only for sulfates, but for total calcium. The largest proportion of the aggregate sulfur stores was carried through the subsoil by the 8-ton treatment and the smallest by the 32-ton addition.

Magnesium carbonate

With increase in treatments, magnesium carbonate caused increases in per cent losses of sulfates from the surface soil. The percentage relationship between sulfate leachings and rainfall sulfur increased with increase in $MgCO_3$ additions for both shallow and deep tanks, each outgo being in excess of the amount brought down in rain water. The impurity factors decreased for both depths with increase in treatment. The sulfate outgo from the shallow tanks was close to 40 per cent of the total available sulfur.

With increase of treatment from 8 to 32 tons, there occurred an increase in percentage relationship of deep-tank sulfate losses to the aggregate amount carried by soil and subsoil. The relationship was quite close, however, for the 32- and the 100-ton additions. The 8-ton rate caused an SO_3 loss about one-fifth of the aggregate of all sulfur supplies, while losses of approximately 27 per cent came from both the 32-ton and 100-ton additions.

Limestone

With the maximum from the 8-ton addition and the minimum from the 32-ton addition in the shallow tanks, each limestone treatment caused a sulfate loss of more than 50 per cent of that possible from the soil. The same order held for relationship of sulfate outgo to rainfall sulfur. In terms of per cent of the aggregate of available sulfur both 8 and 100 tons showed losses greater than the loss from the 32-ton treatment.

The sulfates passing through the subsoil from this treatment are expressed as 17.4, 19.2, and 20.8 per cent of the sulfur carried by both soil and subsoil, in the order of 32-, 8-, and 100-ton treatments. The same order prevails in the losses of 14.4, 15.7, and 17.2 per cent of the respective aggregates of all sources of sulfur.

Dolomite

Increase in the dolomite treatments caused the surface soil to suffer increased losses, 60.0, 67.4 and 98.9 per cent of the amount originally present, having come from the three respective rates. The same holds true as to relationship to the constant amount of rain-water-sulfur content. The 100-ton addition is the only one of 46 tanks which gives a sulfate outgo more than double the amount precipitated by rainfall. The order of per cent relationship is reversed, however, when the actual amounts of sulfur losses are calculated on the basis of aggregate of sulfur supplies, because of the increasing amount of sulfur added as treatment impurities. The factors which express ratio between outgo and impurities decrease with increase in addition.

The ratio of sulfate outgo to combined sulfur content of soil plus subsoil increases with increase of treatment in the deep tanks. The sulfate content of the leachings is less than that of the rainfall in the case of the 8-ton deep tank, but greater for both the 32- and 100-ton rates, the heaviest treatment giving the larger excess. Expressed as per cent of the total available sulfur, the deep tanks give practically the same figures for the 8-, 32-, and 100-ton additions, although the actual amount of sulfate outgo from the latter addition is about twice that from either of the other two. This relationship obtains in spite of the fact that the maximum sulfate came from the 100-ton incorporations, because of the larger residual of unoxidized sulfide impurities.

Magnesite

Increase in magnesite additions did not cause a consistent increase in the fraction of surface-soil sulfur, nor that of rainfall sulfur, which appeared in the leachings. Each of the shallow magnesite tanks lost about 36 per cent of the potential sulfates from soil, treatment, and precipitation.

The 8-ton magnesite addition forced a sulfate loss from the deep tank of about one-sixth of that available from both soil and subsoil and but 79.2 per cent of the sulfate content of the rainfall. The same treatment induced a loss of SO_3 equivalent to only 13.9 per cent of the sulfur derived from all four sources. Both the 32- and 100-ton additions caused a sulfate movement through the subsoil of about one-fourth of the sulfates possible from the stores carried by both surface soil and subsoil and about 20 per cent more than that precipitated by rain. Coincident with the increase in rate of treatment, there occurred a decrease in the factors which expressed the relation between outgo and actual amounts of sulfur added through treatment impurities.

THE OXIDATION OF ZINC SULFIDE CARRIED BY DOLOMITE

In noting the fact that the dolomite treatment was more active than limestone and magnesite in accelerating the outgo of sulfates from the shallow tanks, mention was made of the sphalerite content of the dolomitic limestone.

It was also observed that this disparity in outgo increased with increase in rate and that the maximum of all sulfate leachings came from the 100-ton addition of dolomite. It was assumed that the excesses from the dolomite were due to the oxidation of the zinc sulfide carried by the dolomite. Such oxidation was assumed to be attributable to both chemical and bio-chemical activities. Since the preparation of this manuscript an article bearing upon sphalerite oxidation has been contributed by Rudolfs and Helbronner (9). These workers state: "Apparently as the result of chemical reactions a small amount of zinc sulfide was converted into zinc sulfate" and "However, the inoculated cultures made far more zinc sulfate than the uninoculated mixtures; . . . . ". They further found a steady increase in relative acidity, fluctuations in pH values, and no inhibition from the increased concentrations of sulfofication end products. In our own results of medium has always been alakline for each of the three additions because of the excess of dolomite. Therefore, while the sulfofying organisms may best function in an acid medium, it must be concluded that they also function in one of alkaline reaction, if the excesses of sulfates derived from the dolomite treatments are to be considered as having been generated in the main by bacterial action. The sulfate leachings from the dolomite treatments in the shallow tanks were 1271, 1428, and 2093 pounds of SO_3 as the totals for 8 years from the 8-, 32-, and 100-ton additions, respectively. These three amounts were derived from a soil and rainfall constant of 3149 pounds of SO_3 plus 701, 2804, and 8763 pounds of SO_3 supplied by the respective dolomite additions. The sulfate losses from the surface soil were generally more extensive during the first two years. The losses for the first four years were 66.7, 64.3, and 55.1 per cent of the respective 8-year totals for the additions at the rate of 8, 32, and 100 tons. It can not well be assumed, however, that the major fractions of the sulfate leachings were derived from the sphalerite content of the finely ground dolomite unless the dolomite were considered as differing from the other carbonates and as having no effect upon the oxidation of native soil organic sulfur. For both the precipitated and the native forms of calcium and magnesium carbonates caused a marked acceleration in the outgo of sulfates and a large part of each increase was necessarily derived either from the native sulfur content of the soil or from the rainfall, or from both. When the activities of the organisms responsible for the sulfofication of the sphalerite are established for alkaline calcic-magnesic media containing also neutral calcium and magnesium salts, it will be easier to draw conclusions as to the relative proportions of chemicaland bio-chemical oxidations of sphalerite which were responsible in part for the dolomite-induced sulfate leachings reported in this study.

SUMMARY

An 8-year study of annual sulfate leachings from tanks containing surface soil and surface soil plus subsoil, as influenced by nine different calcic and magnesic materials in different amounts, was carried out by the use of forty-six field lysimeters.

Comparison of treatments disregarding sulfur sources

At the 8-ton rate, all seven materials, CaO, MgO, $CaCO_3$, $MgCO_3$, 100-mesh limestone, dolomite, and magnesite, materially increased the loss of sulfates from the surface soil. Compared with initial annual outgo, there was a distinct diminution in all losses from the surface soil after the first year. The losses from the treated tanks, however, continued to be greater than those from the control. Only fractions of the increases of the initial year passed through the subsoil, but represented distinct increases over the meager leachings through the subsoil of the control. The tendency of the subsoil losses was to increase from minimum initial outgo, the amount of increase depending upon the solubility of the alkali-earth addition. The differences between the 8-year outgo of SO_3 from surface soil and from surface soil plus subsoil were greatest in the case of the native carbonate treatments.

At the 32-ton rate the distinctly depressive influence of CaO is shown in contrast to the activating influence of MgO and the carbonates. The MgO and $MgCO_3$ admixtures were the most active at first. The sulfate losses from the surface soil decreased for all treatments, save CaO, after the initial year. The losses of the second and third years and many of those of the succeeding years, were, however, still in excess of losses from the control tank. The sulfate losses from the subsoil tanks were greatest for the MgO and $MgCO_3$ treatments during the second and third years. The smaller losses from less soluble materials and CaO did not become maximum until the third year, or the fifth year, and in three cases, even later. The 8-year totals from surface soil and from subsoil tanks were less for the CaO treatment than for the others. The relationship between the surface-soil 8-year totals and those from the soil-subsoil were governed by the solubilities of the several additions. Wollastonite was found to increase the losses much more than serpentine.

At the 100-ton rate, CaO was found to be exceedingly effective in stopping losses from the surface soil, but after the fourth year the heavy addition became active in forcing sulfates from the subsoil zone. All other additions increased the surface soil losses to excessive amounts during the initial year, the MgO and $MgCO_3$ treatments again being most active in this regard. Even with a decided fall-off during the second and third years, the losses during each of these two years were still largely in excess of the loss from the surface soil control. The maximum surface-soil outgo for the 8-year period was caused by dolomite which materially supplemented the sulfur stores available for oxidation because of its content of sphalerite.

The MgO and $MgCO_3$ treatment were again the first to force surface-soil sulfates through the subsoil, the largest amounts coming during the third year. The less soluble materials showed increased losses from the subsoil during the fifth and sixth years and even through the seventh year. The more penetrating $MgCO_3$ and MgO additions were responsible for large losses sulfates from the subsoil zone, and thus caused soil-subsoil totals in excess

of those from the corresponding surface soil. The remaining four of the six more active materials caused larger 8-year losses from the surface soil than from the surface soil plus subsoil.

The influence of magnitude of treatment was found to vary. Increase in applications of burnt lime was followed by progressive depression of surface-soil sulfate outgo, but only the heaviest application depressed the total below that of the control. Compared with the increases from the other six oxide and carbonate additions in the deep tanks, increase in amounts of lime brought increased, though not progressive, depression. But in spite of this effect the sulfate outgo for each treatment was largely in excess of that of the subsoil-tank control.

Increased treatments of MgO and $MgCO_3$ caused progressive increases in both initial and total sulfate losses from the surface soil. The same held true in regard to soil-subsoil losses.

The chemical and biochemical factors responsible for the depressive action of CaO were considered in connection with calcium hydroxide concentrations of leachings and the solubility of freshly precipitated $CaSO_4$ in such concentrations.

No consistent increase in sulfate outgo from the surface soil resulted from increase in rates of treatment of $CaCO_3$, limestone, or magnesite, but increased loss of sulfates, with increased treatments of dolomite in both surface soil and subsoil tanks was probably due to increasing amounts of sphalerite.

The sulfate increases in the subsoil leachings were found to be more dependent upon the solubility than quantity of the alkali-earth additions and ran parallel with increased concentration of the applied base in leachings. While increased MgO, $MgCO_3$, and dolomite additions gave decided progressive increases in total SO_3 lost from the subsoil, the same did not hold for $CaCO_3$ and limestone. Although a material increase in sulfate losses followed the increase of magnesite from 8 tons to 32 tons, little additional outgo resulted in the further increase to 100 tons.

The systems $MgCO_3$-$MgSO_4$-H_2O and $CaCO_3$-$CaSO_4$-H_2O were affected differently by the treatments with MgO, $CaCO_3$, and $MgCO_3$ and they differed in rapidity of outgo from the subsoil. Greatly increased sulfate leachings and increased alkalinity were induced first by the 32-ton-equivalent additions of both MgO and $MgCO_3$, though the totals came in order of treatment. But the totals of both sulfates and calcium were less from the 32-ton $CaCO_3$ treatment than from either 8- or 100-ton additions.

Effect of treatments as related to sources of sulfur

Relationships were calculated for each total outgo to each of the several sources of sulfur; viz., soil, soil and subsoil, treatment impurities, and rainfall. Except CaO at 32- and 100-ton rates, every treatment at each rate caused a loss of more than one-half of the original sulfur content of the surface soil. With the same exception, all treatments caused losses in excess

of the rainfall sulfur. All treatments at the 8-ton rate induced sulfate losses approximating 35 per cent of the sulfur available from all sources. The same was true of all surface-soil losses from the 32- and 100-ton additions of MgO, $CaCO_3$, $MgCO_3$, limestone, and magnesite. Expressed as per cent of the total sulfur available, the sulfate leachings from the surface soil tanks decreased with increase in treatments of both CaO and dolomite. The burnt lime caused actual as well as per cent decreases. But in spite of a marked progressive increase in outgo parallel with increase in dolomite treatment, the outgo appears as a low per cent of the total available sulfur because of the augmented sulfur supply and unoxidized residues of sphalerite impurities.

The sulfur loss from each of the seven treatments, at each rate was less than the amount originally present in the soil plus subsoil. With the exception of CaO and limestone at all rates, dolomite and magnesite at the 8-ton rate and $CaCO_3$ at the 32-ton rate, each of the seven materials caused subsoil sulfate leachings in excess of the amount of SO_3 carried by the rainfall. The respective relationships between subsoil losses and totals from all sources may be considered best in detail by reference to the last column of table 8.

It was shown that unaltered subsoil stopped large amounts of sulfates and that the influx of calcium and magnesium salts served to diminish or even overcome this property and in some cases to push sulfates through the subsoil.

The value of parallels of tanks with and without subsoil is emphasized in the determination of periodicity and magnitude of sulfate generation in the surface soil; the increased or decreased tendency of the subsoil to permit passage of sulfates as a result of treatment; the subsoil zone as a source of engendered or liberated sulfates; and attainment of balance between the several systems involved in the sulfate concentrations of the leachings.

The sulfate sulfur leached from the untreated soil was less than the amount brought to it by rainfall.

The oxidative processes responsible for the generation of sulfates from zinc sulfide were mentioned and assumed to be of both chemical and biochemical nature, until more data are at hand relative to biological activities in alkaline calcium-magnesium media.

The treatments heavier than the 8-ton equivalent rate may be considered primarily as of academic interest, in showing the divergent effects induced by the several materials applied. But the data from the 8-ton additions may be construed not only as showing the divergent influences of treatment, but also as indicating that the injudicious use of liming materials may rapidly impair the supply of sulfur carried by the surface soil, particularly where the supplementary supplies derived from rainfall are meager in quantity.

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SOIL ACIDITY, AN ECOLOGICAL FACTOR[1]

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INTRODUCTION

Since colorimetric methods were developed for the study of soil extracts there has been an increasing number of observations on the relation of the hydrogen-ion concentration of the soil extract to plant distribution. The general conclusion resulting from these studies has been that a soil of a particular locality has a more or less definite pH value and that plants found upon this soil are frequently those having a preference for that hydrogen-ion concentration.

These studies have been made frequently by testing the surface soil or that about living roots plucked from the soil. It seemed desirable to make a more intensive study of a particular region through a considerable length of time, taking into consideration the pH values of the subsoil and their relation to root distribution.

Subsoil acidity has not been without investigators. Wherry (13), working at Millsboro, Delaware, in March 1919, found that in digging down into sand beneath upland peat the acidity decreased markedly. Two years later Arrhenius (2), making borings about Bahtim and Giza in Egypt in some cases to a depth of 300 cm., found that the surface soil was alkaline but that the alkalinity decreased with depth; finding at Bahtim, however, an increase in pH values from surface to a certain depth followed by a decrease. Salisbury (10), in England, has also found a decrease in acidity of the subsoil of woodlands.

SOILS AND METHODS OF TESTING

A convenient locality was found in Chester County, Pennsylvania, about the village of Paoli. Within a radius of five miles there are five soil types with a number of diversified phases; Hagerstown (limestone), Chester (granitic), Manor (schistose), Dekalb (sandstone) and Conowingo (serpentine). A description of these soils and their location will be found in an earlier paper (6). Comparable areas were selected, representing as far as possible the average condition of that soil type and having as far as possible among themselves the same degree of slope, drainage and exposure. A large proportion of the tests were made in wooded regions which were as nearly in an undisturbed condition as could be found, while many tests were made in cultivated fields as well.

[1] A thesis presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Work was begun in November 1920. Originally only the surface soil was tested, by the colorimetric method described by Wherry (12). In the summer of 1921 it was decided to make careful tests on the subsoil. The soil auger used, consisted of a 1.5-inch wood auger the shaft of which was threaded and fitted to 50 cm. joints of gas-pipe and a handle. This could be carried conveniently in the field and could be operated to a depth of two metres, though this depth was not found except in Hagerstown loam.

In boring, care was taken that the samples should not be contaminated by soil of higher levels. A bit of the core from successive 15-cm. levels was pressed into a glass test-tube 100 x 15 mm. to a height corresponding to that of 5 cc. of water; the tube was corked and carried to the laboratory. Here distilled water (conductivity 2×10^{-6}) was added to a level equivalent to that of 15 cm. of water; the soil and water were then thoroughly stirred with a clean glass rod, and the suspension was allowed to settle, requiring usually from two to twelve hours. The entire interval between taking the sample and testing was seldom more than twenty-four hours.

Clear extracts could then be tested directly, using 1 cc. of the extract and comparing with standards as described by Clark and Lubs. Since the extracts were frequently turbid, a comparator was constructed by which the turbid extract might be compared with the standard which was screened by a similar turbid extract, viewed by electric light screened by blue glass. When very turbid the extract was diluted with distilled water to two or three times its volume, giving but a small error.

TABLE 1

Relation of productivity to soil reaction

SOIL TYPE	CHARACTERIZATION BY SOIL SURVEY	AVERAGE REACTION
		pH
Hagerstown	"exceptionally well adapted to crop production"	6.92
Chester	"well adapted to crop production"	6.53
Manor	"of considerable less value than Chester"	6.15
Dekalb	"not very productive"	5.71
Conowingo	"very poor"	5.38

RESULT OF SOIL TESTS

Surface soil tests had shown that a general average pH could be assigned to comparable areas of each loam, and these are given in table 1, together with a characterization of each soil made by the United States Department of Agriculture soil survey in 1906 (15). Correspondence between degree of fertility and pH value is evident.

Results of boring tests are given in table 2, in which the serial number of the test is given in the left-hand column, the depth in centimeters at the top and the average acidity at the bottom. Tests were not made closer than pH 0.1. All tests were made colorimetrically and have not been checked with the hydrogen electrode. Tests on Dekalb and Conowingo loams may be somewhat in error because indicators used with these soils were methyl red and cresol purple, which indicators are often not in agreement. Two indicators were always employed in testing and in some doubtful cases three.

Relations between average values determined from table 2 are made more evident by figure 1. It is seen at once that in most cases the curve does not

TABLE 2

Reaction of soil types studied

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE								
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.	120 cm.
	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H
Hagerstown loam									
332	6.9	...	6.8	6.6	6.6	6.8	6.8	6.8	7.0
341	7.1	...	6.8	...	6.7				
454	7.0	...	6.4	6.6					
816	7.0	7.3	7.5	7.4	7.5	7.5	7.4	7.4	
824	7.0	7.4	7.3	7.3	7.5	7.4			
830	7.0	...	7.4	7.5	7.5				
735	7.0	6.7	7.2	7.2	7.0	7.0	7.1	7.2	
743	7.0	6.8	6.7	7.0	7.2	...	7.2	7.2	7.3
752	7.0	6.8	6.8	7.0	7.2	7.2	7.3	7.4	
882	7.1	7.0	7.0	7.2	7.0				
892	7.0	7.0	7.0	7.0					
897	7.0	6.5	...	7.0	7.0				
974	7.0	6.6	6.8	7.0	7.0				
990	7.0	6.5	6.0	6.2					
994	7.0	6.8	7.0	...	7.0				
999	6.6	5.8	6.4	6.6	6.6				
1004	6.8	6.4	6.8	6.8	7.0				
1009	6.5	6.5	5.8	6.0	6.2				
1019	7.3	6.9	7.0	7.1	7.0				
1024	7.2	6.8	7.0	7.0	6.9				
1029	7.0	6.8	6.9	6.9	7.0				
1220	7.4	6.8	7.1	6.4	6.8				
1225	7.3	7.4	7.3						
1228	7.3	7.2	7.3	7.4	7.4				
1226	7.2	6.2	6.5	6.5	6.5	7.0	7.0		
1273	7.0	6.6	...	6.8	7.0	7.0	7.0	7.0	
1281	6.6	6.4	7.0	7.3	7.4	7.0	7.0		
1335	6.4	6.0	6.0	5.8	5.8	5.9			
1341	6.4	6.0	6.0	6.0	6.0				
1346	6.2	6.0	5.8	6.0	6.0				
1381	7.0	...	6.8	6.7	7.0				
1439	6.8	6.8	6.5	6.5	6.5				
1444	6.8	6.6	6.5	6.5	6.5				
1449	6.8	6.8	6.6	7.0	7.0				
1553	7.0	7.0	6.8	7.0	7.0				
1568	7.0	6.6	6.6	7.0	7.0				
1558	6.7	6.5	6.6	6.8	7.0				
Av.	6.9	6.6	6.7	6.8	6.8	6.9	7.1	7.1	

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE								
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.	120 cm.
	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H
Chester loam									
428	5.6	4.4	4.4	5.0					
433	...	4.4	4.4	5.1	5.2	5.1	5.8		
440	...	5.0	5.0	...	6.0				
499	6.2	6.4	6.4	6.4	6.4	6.4	6.0	6.2	
506	6.8	5.9	6.3	6.8	6.6				
511	7.0	6.2	6.2	...	6.2	...	...	6.6	
519	7.0	6.4	6.5	6.6					
523	7.0	6.4	7.0	6.4	6.4	6.6	6.8		
836	6.6	...	6.0	6.5	6.6				
841	6.8	6.2	6.3	6.4	6.8				
563	6.2	6.2	6.4	6.8					
568	6.8	...	6.4	6.4	6.6	6.5	6.5	6.6	
583	7.0	6.5	6.4	6.6					
587	7.0	...	6.5	6.1					
591	6.8	6.4	6.5	6.7	6.8	6.8			
607	5.8	5.4	6.0	6.1	6.1	6.1	5.8	5.8	
617	...	5.6	5.8	6.0	6.1	6.1	6.2		
624	6.5	5.4	5.8	5.9	6.1	5.8	6.0	5.8	
1031	6.5	5.6	6.2	5.8	6.1				
1035	6.5	5.6	5.8	5.8					
1039	6.5	5.6	6.5	6.8	7.0				
1044	6.8	6.0	6.1	6.2	6.2				
1049	7.0	6.6	5.6	6.4	6.8				
1054	6.5	6.2	6.4	6.4	6.2				
1049	6.2	6.0	6.4	6.5	6.6				
1064	6.0	5.6	5.8	6.0	6.2				
1070	6.0	5.8	5.5	5.6	5.6				
1075	5.5	5.4	5.6	5.6	5.7				
1080	7.0	6.1	7.0	6.9	6.8				
1085	6.8	6.8	6.3	6.4	6.8				
1090	6.5	6.6	7.0	7.0					
1246	6.8	6.2	6.2	6.3	6.4				
1251	6.0	6.1	6.2	6.3	6.4	6.6	6.6		
1258	6.9	5.8	6.1	6.1	6.1	...	6.4	6.5	
1317	6.2	5.4	5.6	5.6	6.1	6.0			
1323	6.4	5.6	5.8	6.0	6.0				
1329	5.6	5.7	5.8	5.8	6.0	6.0			
1409	6.5	5.4	5.4	5.4	5.6				
1414	6.4	...	5.8	5.6	6.0				

TABLE 2—*Continued*

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE								
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.	120 cm.
	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H
Chester loam—Continued									
1419	6.3	6.3	6.2	6.0	6.0				
1484	7.0	6.8	6.8	7.0	7.0				
1489	7.0	...	6.8	6.8	7.0				
1494	7.0	6.8	6.9	6.9	7.0				
1568	6.8	6.2	6.7	6.8	6.8				
1573	7.0	6.6	6.5	6.7	6.8				
1578	6.1	5.8	6.4	6.8	...				
Av.	6.5	5.9	6.1	6.2	6.2	6.2	6.2	6.2	
Manor loam									
370	...	5.2	6.2	6.6	6.4				
375	6.0	6.2	6.2	6.6	6.4	6.6			
381	6.1	5.6	6.7	6.8	7.0	6.9	6.8		
388	...	...	5.2	5.0	5.0	5.0	5.0		
395	...	5.2	5.5	5.1	5.2				
400	...	4.7	4.7	5.0	5.0	5.2	5.4		
676	7.0	6.2	6.5	6.8	6.8	6.8	6.8		
686	6.8	5.6	6.6	6.8	6.8				
867	6.5	5.7	6.5	6.5	6.6				
872	6.4	5.8	6.6	6.8	6.5				
919	7.0	6.1	5.9	6.3	6.5				
924	7.0	6.1	5.9	6.3	6.5				
1094	5.2	5.0	5.0	5.1	5.1				
1099	5.8	5.2	5.0	5.0	5.0				
1106	5.6	5.5	5.7						
1114	6.2	5.8	6.4	6.5	6.5				
1119	6.6	6.5	6.0	6.0	6.4				
1134	5.1	4.8	4.9	4.9	5.2				
1301	5.4	5.6	6.1	6.1	6.2				
1306	5.4	5.1	5.3	5.4	5.5				
1311	5.6	5.5	5.7	5.9	6.1				
1366	5.8	5.4	6.0	6.0	6.0				
1371	5.8	...	6.5	6.5	6.5				
1376	6.1	6.1	6.0	6.0	5.8				
1454	6.7	6.2	6.6	6.9	6.8				
1459	6.6	6.2	6.9	6.9	6.8				
1464	6.6	6.4	6.8	6.8	6.8				
1579	6.8	6.4	6.6	6.6	6.8				
1584	6.6	5.8	6.0	6.8					
1588	5.8	6.0	6.0	6.2	6.4				
Av.	6.1	5.7	5.8	6.1	6.2				

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE								
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.	120 cm.
	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H	*p*H
Dekalb loam									
352	5.4	5.2	5.4	5.4	6.0				
472	5.8	5.8	6.0	6.2					
476	5.4	5.2	5.2	5.2	5.2	5.2			
487	5.9	6.2	6.4	6.4	6.4				
492	6.0	6.5	6.4	6.2	6.0				
710	6.1	5.7	5.6	5.6	5.8	5.7	6.0		
717	5.0	...	5.2	5.1	5.2	5.5			
723	5.0	5.6	5.4	5.2	5.2				
785	5.7	5.6	5.7	5.7	5.6	5.6			
792	5.6	5.4	5.4	5.8	5.8				
760	5.7	5.2	5.0	5.0	5.0	5.0	5.0		
767	5.6	5.0	5.0	5.0	5.4	5.7	5.6		
774	5.9	5.4	5.6	5.4	5.8	5.8	6.0		
781	5.6	5.4	5.6	5.7					
897	5.4	5.4	5.6	6.0	6.5				
902	5.3	5.4	5.9	6.1					
906	5.8	5.4	5.6	5.7	6.1				
911	6.1	6.6	6.6	6.4					
929	5.8	5.6	5.6	5.7					
934	5.4	6.0	6.2	6.4	6.5				
939	6.0	6.0	5.9	6.0	6.0				
944	5.8	6.0	5.0	5.6	5.7				
954	5.4	5.4	5.2	5.2	5.2				
959	5.8	5.8	6.0	6.0	6.0				
963	5.7	5.4	5.3	5.3	4.9				
968	5.8	5.4	5.8	6.1					
1207	6.0	6.0	6.3	6.4	6.2				
1212	6.3	6.1	6.3	6.4	6.4				
1311	5.6	4.9	4.9	5.2	5.2				
1356	5.6	5.2	5.0	5.1	5.2				
1361	5.6	5.4	5.4	5.8	5.6				
1396	5.7	5.3	5.3	5.4	5.6				
1401	5.7	5.3	5.3	5.3	5.5				
1406	6.1	5.4	5.4	5.5	6.1				
1429	6.1	5.4	5.4	5.7	5.7				
1434	6.1	6.4	5.4						
1593	5.4	5.8	6.0	6.2	6.4				
1598	6.2	6.4	6.4	6.6	6.6				
1603	5.8	6.0	5.6	6.4	6.6				
Av.	5.7	5.6	5.6	5.7	5.7				

TABLE 2—*Concluded*

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE								
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.	120 cm.
	pH	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
Conowingo loam									
418	4.6	4.8	5.0	5.8					
422	4.6	4.4	5.6	5.8					
549	5.4	5.4	5.6	5.8	6.2				
557	5.4	6.2	6.1	6.2	6.4	6.4			
530	5.6	5.6	5.8	6.1	6.2	6.1			
541	5.6	5.6	5.8	6.1					
549	5.4	5.4	5.6	5.8	6.2				
557	5.4	6.2	6.1	5.8	6.4	6.4			
632	5.1	5.0	5.2	5.2	5.7	5.8			
639	5.4	4.9	5.2	...	5.8	6.0			
646	6.0	5.8	5.8	5.8	6.2				
653	5.8	5.4	6.2	6.4	6.4	6.6			
659	6.0	6.0	6.4	6.4	6.1	6.1			
847	5.0	5.6	5.7	5.8	6.0				
857	5.0	5.4	5.6	5.8	6.2				
1139	5.2	5.6	6.0	6.5	7.0				
1144	5.4	5.8	5.8	6.0	6.2				
Conowingo loam—Continued.									
1149	5.8	6.0	6.0						
1152	4.8	5.0	6.0	6.5	6.2				
1157	5.0	4.8	5.0	5.0	6.0				
1162	5.6	5.6	5.8	6.0					
1166	6.1	5.7	6.5	6.5	6.5				
1171	5.2	5.6	5.8	5.6	6.0				
1233	5.4	5.8	6.0	6.0	6.3				
1238	6.1	4.4	5.1	5.3	5.3	5.5			
1294	5.2	...	5.3	5.5					
1469	5.4	5.6	5.8	5.8	5.8				
1474	5.4	5.0	5.6	5.8	5.8				
1608	5.4	6.2	6.4	6.4	6.4				
1613	5.8	5.9	6.0	6.4					
1617	4.8	5.4	5.8	6.2	6.4				
Av.	5.3	5.4	5.7	5.9	6.5				

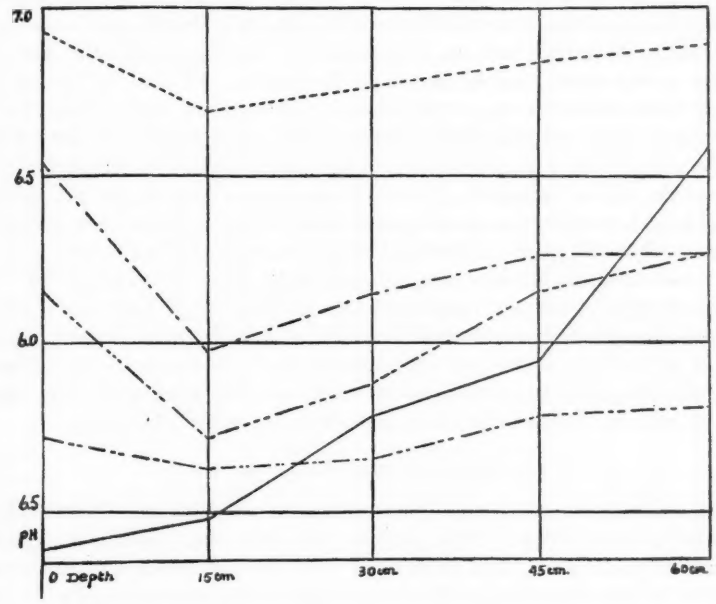

FIG. 1. GRAPHS SHOWING VARIATIONS IN ACIDITY WITH DEPTH

---------- Hagerstown Loam.
—————— Chester Loam.
—·—·—·— Manor Loam.
—— —— —— Dekalb Loam.
———— Conowingo Loam.

show a steady rise from the acid side towards neutrality as most previous work would indicate but that there is a drop in pH to about 15 cm., rising then at lower levels towards the neutral point,—a type of curve found by Arrhenius at Bahtim, Egypt. This drop is small in limestone soil; in the others we find that the successive curves between 0–15 cm. describe as it were an arc—somewhat like an opening fan—as the surface soil acidity increases faster than that of the subsoil, until the curve shows a steady decrease from surface downwards. In all cases there is a rise of the pH value at lower depths towards neutrality; this is markedly so in Conowingo. A general statement, then, regarding subsoil acidity can not be made for all but for particular kinds of soil, except that at lower depths the reaction approaches neutrality.

MONTHLY SOIL TESTS

Values obtained from monthly tests made in the same locality for one year are given in table 3. The reader will note that there is no fixed pH value for any particular portion of soil, and that the change from the mean is not large. It amounts at times, however, to pH 1.0 during the growing season, in the subsoil as well as at the surface, hence the plants growing in these places can not be appreciably injured by small variations in acidity.

It will also be seen that during the late summer, from July to October, there is a continual increase in the acidities recorded, except in Dekalb and Conowingo for August (these tests were made one week later than the others in that month, after a rain storm), and in Manor for September. All tests in September were made within two days, after a heavy rain-storm by which Manor loam seems to have been differently affected. The three months on the whole were marked by a long-continued drought; with coming of late autumnal rains the acidity decreased. Then, with coming of freezing, the pH values was again lowered to rise once more on thawing; we see in Hagerstown for February, while still frozen, a lower pH while the other soils had thawed.

Under field conditions drying is apparently often accompanied by increased acidity, but not invariably; thus in Conowingo loam tests made after a heavy rain showed increased acidity, whereas drying in the next month to a pulverulent powder was accompanied by a decreased acidity. These conclusions might be compared with those found by Burgess (3) viz., that acid soils were little changed in acidity by drying in the laboratory.

DISCUSSION OF RESULTS OF SOIL TESTS

The significance of the type of curve found is not apparent. From studies made in woodlands one might consider that decay and leaching of organic acids from leaves and plant debris might cause an acid condition in the subsoil while the salts remaining at the surface might cause a lessened acidity (5). A recent paper (9) attempts to show that facies of a formation determine the reaction of the soil upon which they grow by the different amounts of acid-formers liberated from their decaying leaf-litter.

But the same type of curve is found under old sod where there should be but little leaching, and in cultivated fields where there should be almost none.

TABLE 3

Results of monthly tests, April, 1922–March, 1923

MONTH	REACTION AT VARIOUS DISTANCES FROM SURFACE				
	Surface	15 cm.	30 cm.	45 cm.	60 cm.
	pH	*pH*	*pH*	*pH*	*pH*
Hagerstown loam					
April	7.0	6.9	6.7	6.6	6.8
May	7.0	7.3	7.3	7.4	7.5
June	7.0	6.6	6.9	7.0	7.1
July	7.0	6.7	7.0	7.0	7.0
August	7.0	6.6	6.6	6.6	7.0
September	6.6	6.3	6.3	6.4	6.6
October	7.1	6.8	6.6	7.0	6.9
November	7.3	7.0	7.2	6.9	7.1
December	6.4	6.0	6.0	6.0	6.0
January	7.0	...	6.8	6.7	7.0
February	6.8	6.8	6.5	6.6	6.6
March	7.0	6.8	6.8	6.8	7.0
Chester loam					
April	6.2	6.0	6.3	6.4	6.5
May	6.8	6.2	6.4	6.5	6.4
June	6.0	5.9	6.2	6.6	6.7
July	6.6	5.8	6.1	6.0	6.3
August	6.6	6.3	6.1	6.4	6.5
September	6.0	5.8	6.0	6.0	6.1
October	6.8	6.5	6.7	6.8	6.8
November	6.7	6.0	6.1	6.2	6.3
December	6.1	5.6	5.7	6.3	6.3
January	6.4	6.3	5.8	5.7	5.8
February	7.0	6.8	6.8	6.9	7.0
March	6.9	6.4	6.6	6.8	6.8
Manor loam					
April	6.3	5.4	5.6	5.8	5.8
May					
June	6.2	5.5	6.0	6.1	6.2
July	6.4	5.7	6.5	6.6	6.5
August	5.6	5.2	5.2	5.0	5.0
September	6.2	5.9	6.0	6.2	6.3
Manor loam—Continued					
October	5.6	5.4	5.6	5.7	5.8
November	...	...	...	...	...
December	5.5	5.3	5.7	5.8	5.9
January	5.9	5.7	6.0	6.0	6.0
February	6.6	6.2	6.8	6.8	6.8
March	6.4	6.0	6.2	6.4	6.6
Dekalb loam					
April	5.8	5.4		5.0	4.8
May	5.6	5.7	5.6	6.0	5.7
June	5.4	5.7	5.6	5.4	5.4
July	5.7	5.3	5.3	5.3	5.5
August	5.8	5.9	5.9	6.0	6.2
September	5.6	5.7	5.4	5.6	5.6
October	5.9	5.4	5.8	5.7	4.9
November	6.1	6.0	6.3	6.4	6.2
December	5.6	5.1	5.1	5.3	5.3
January	5.7	5.3	5.4	5.4	5.5
February	6.1	5.4	5.4	5.6	5.9
March	5.8	6.0	6.0	6.4	6.5
Conowingo loam					
April	5.6	5.7	5.8	6.0	6.2
May	5.5	5.9	5.8	6.0	6.2
June	5.6	5.4	5.7	5.7	5.9
July	5.0	5.5	5.6	5.8	6.1
August	5.4	5.8	5.9	6.2	6.6
September	5.1	5.1	5.6	5.9	6.1
October	5.9	6.0	6.6	6.0	6.3
November	5.6	5.8	6.0	6.4	6.5
December	5.4	5.3	5.2	5.4	5.5
January	5.0	4.4	5.2	5.4	5.5
February	5.4	5.0	5.6	5.8	5.8
March	5.2	5.8	6.0	6.3	6.4

Table 4 gives the averages of results obtained from forty series of tests made in open fields immediately adjacent to the wooded areas studied for the soil types, made monthly from July to February inclusive.

The curve might result from chemical reactions and adsorption phenomena so that the actual acidity might not appear at the surface, and in the subsoil acid salts set free from their adsorbed condition by an excess of organic acids might be gradually neutralized by basic substances arising from below in the ground water.

From a study of the distribution of microörganisms in the soil as given by numbers of workers (7) it seems that in general these are found chiefly in the first 16 cm. of soil, with comparatively few below 90 cm. It would seem also that bacteria, protozoa and some algae are to be associated with a soil reaction near neutrality while fungi are more frequently found under acid conditions. It was shown further by Moore (8) that in some soils bacteria had been found at the surface whereas fungi were in lower levels of the same soil. In the soils studied fungi were practically absent from Hagerstown loam, not uncommon in Chester, becoming very abundant in Conowingo loam where they formed with roots a dense mycorhizal mass knitting the leaf-litter together. While microörganisms may have no relation to soil

TABLE 4

Average reactions of cultivated soils

SOIL TYPE	REACTION AT VARIOUS DEPTHS FROM SURFACE				
	Surface	15 cm.	30 cm.	45 cm.	60 cm.
	pH	*pH*	*pH*	*pH*	*pH*
Hagerstown	6.84	6.62	6.54	6.68	6.77
Chester	6.36	6.06	6.34	6.36	6.44
Manor	6.15	5.92	6.11	6.26	6.31
Dekalb	5.94	5.85	5.86	6.12	6.25
Conowingo	5.84	6.03	6.06	6.40	....

acidity except as it forms one of the ecological factors to which they are subject, an interesting problem is nevertheless opened for investigation.

RELATION TO ROOT DISTRIBUTION

Soil acidity affects the plant through the roots and study of root distribution is consequently important in any investigation of the effects of hydrogen-ion concentration on vascular plants. There have been excellent works on root distribution, as that of Weaver (11), who traced out entire root systems with the utmost care, finding that herbs and shrubs of the forest floor are relatively shallow-rooted, that almost without exception the bulk of the absorbing system lies within the surface eighteen inches of soil and that even roots of trees have many shallow branches.

The writer has made some observations on roots of woodland species by digging a trench two meters long, a half-meter wide and down to loose rock. Study of tree roots is more difficult in order to make generalizations. Numerous quarries of the region were studied, where freshly loosened faces are con-

stantly exposed, and neatly exhibit the root distribution not only of herbs and shrubs but also of trees. Trees of various species uprooted by windstorms were also observed. All observations indicated the same general conclusion, that most of the absorbing system of woodland plants is near the surface. It seemed questionable even whether trees in general have deeply penetrating tap-roots, and in two soil types they would be practically impossible since bed-rock occurs within two meters of the surface.

An example of root distribution under "average" conditions (in Manor loam) is shown in figure 2, drawn to scale from a surface exposed by an excavation. Most of the absorbing system is within the first 12 cm. with another stratum from 30 to 70 cm. and only occasional fibrous roots below,

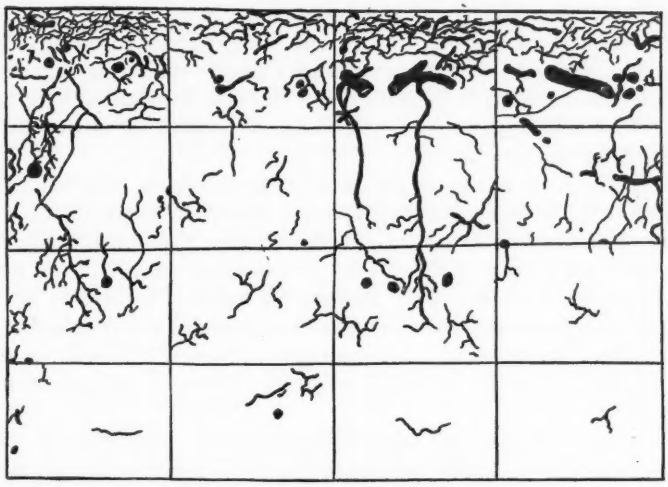

FIG. 2. ROOT DISTRIBUTION IN MANOR LOAM

Scale: 1 mm. = 2 cm.

while there is a layer of conducting roots at 15 cm. Absorbing roots would seem to be associated here with soil nearer neutrality. Dekalb soil is shallower and the root system is more compressed, still more so in Conowingo. In Chester and Hagerstown loams apparently absorbing roots are spread deeper in the soil.

Mycorhiza were found abundantly in the lower part of the leaf mold and in the soil (of the above example) to a depth of 15 cm. where they formed a network of white hyphal strands. Mycorhiza were most abundant in Conowingo woodland soil, least abundant in Chester and absent from Hagerstown. Where they were most abundant the reaction curve showed no depression but steady rise from a low pH, a condition found also in sterile pastures.

PLANT DISTRIBUTION

The significance of plants as indicators of soil conditions described by different writers from the beginning of such work has been summarized to 1919 by Clements (4) who has also indicated the relation of various ecological factors to plant species. Of these factors, hydrogen-ion concentration is one. Various factors have been considered as controlling plant distribution; among these relative elevation, degree of shade, slope exposure, soil temperature, soil moisture, soil texture, aeration, carbon dioxide and salt content of the soil, and soil reaction. One has been stressed at one time at the expense of others. In 1920 Arrhenius (1) considered that soil acidity was a primary factor and in 1922 Wherry (14) agreed that soil acidity is of fundamental importance. It would seem that by interaction of many or all of these factors, one of which at some time and in some place may become predominate, there results an ecological environment causing a specific plant association.[2]

This idea of the soil as "a living thing" has been emphasized by Professor John W. Harshberger, to whom the writer is indebted for advice and help during prosecution of this work.

In studying the ecology of the Paoli region the writer, after familiarizing himself with the flora, undertook quadrat surveys in woods of the various soils. A quadrat of 15 meters was chosen since this size is conveniently measured and a block of four quadrats corresponds roughly to the 100-foot quadrat used by some others. Because the region is undergoing suburban change, woodlands often indicate succession stages and quadrat plottings may show quite different results. A comparison of a number is therefore necessary for an appreciation of the real significance of vegetational distribution on that soil.

Facts as to presence and relative abundance of many species on the soil types studied have already been given (6). It is now desirable to present a more detailed comparison of the consocies.

PLANT DISTRIBUTION ON THE SOIL TYPES

Most productive among the soils, Hagerstown loam is largely under cultivation and presents but few areas of woods on any but rocky ledges. Here *Ulmus americana*[3] is the dominant species (with *Acer saccharum* in one region),

[2] The excellent work of Carsten Olsen in Compt. Rend. Labor. Carlsb., v. 15, no. 1, 1923, did not appear in time to be reviewed in this paper. The writer would call attention, however, to emphasis laid upon the necessity of filtration of the soil extract to remove any solid particles which might cause adsorption of the indicator, falsifying the result. But might not the filter paper introduce as serious an error by adsorption? The paper also shows the value of comparing several entirely different soil types, for two similar habitats on one soil type with the same hydrogen-ion concentration may support the same facies, but two similar habitats with the same hydrogen-ion concentration on different soil types may have quite different facies. Hydrogen-ion concentration, then, would not be the controlling factor.

[3] All species names are according to the seventh edition of Gray's Manual.

while *Fraxinus americana* is subdominate and such species as *Juglans nigra, Fagus grandifolia, Quercus rubra, Liriodendron tulipifera, Platanus occidentalis, Prunus Mahaleb* are sparse or may form families. These grow in open formation, often with an overhead draped and luxuriant growth of *Vitis cordifolia* making a deep shade so that but few of the smaller treee are found, as *Celtis occidentalis* and *Prunus virginiana,* while saplings of the trees noted above are frequently killed. *Rhus toxicodendron* grows characteristically over ledges and forms mats of erect branches on open ground. The bush stratum is almost entirely *Benzoin aestivale,* changing to species of *Rubus* where there is an opening permitting light to strike through. Little leaf-mold is present, leaves quickly decay and the soil often becomes dry and pulverulent in late summer. There is a sparse ground cover of *Geum canadense, Agrimone hirsuta, Solidago ulmifolia, Aster cordifolia,* but on moist shaded (usually north-facing) slopes are families of *Polystichum acrostichoides, Aspidium marginale, Thalictrum dioicum, Hepatica triloba, Cicimifuga racemosa, Cheilidonium majus, Dicentra canadensis, Dentaria laciniata, Osmorhiza longistylis, Hydrophyllum virginicum* and *Nepeta hederacea,* though *Stellaria media* frequently forms a wide-spread evergreen mat.

Some of the ledges are occupied by a dense growth of *Juniperus virginiana,* which also occurs scattered in rocky pastures with *Crataegus crus-galli.* Here *Aquilegia cabadensis* is typically found on the ledges, and where there is less soil, *Camptosorus rhizophyllus* and *Pellaea atropurpurea.* Social groups of *Oxalis stricta Plantago virginica* and *Antennaria canadensis* grow in dry pastures among grasses and sedges.

Proceeding to Chester loam we find *Ulmus americana* is still present but sparse, and *Fraxinus americana* is now dominant, succeeding *Castanea dentata,* the blighted chestnut. *Prunus Mahaleb* and *P. pennsylvanicum* are frequent; *Quercus alba, Q. rubra, Q. velutina* and *Liriodendron* are found much as on the preceding loam, while species of *Carya* are better represented, especially by *C. ovata.* But all of these species grow in rather close formation with abundant undergrowth, a second story, of *Cornus florida* and smaller shrubs of *Corylus americana, Benzoin aestivale* and *Viburnum molle. Vitis cordifolia* does not form as luxuriant a growth while *V. labrusca* is more frequent.

More leaf-mold is found with occasional mycorhiza, and moisture is better retained. There are more species of herbs, these forming a close ground cover of *Smilacina racemosa, Sanguinaria canadensis, Asarum canadense, Podophyllum peltatum* and others, later being succeeded by families of *Osmunda Claytoniana, Collinsonia canadensis* and *Aster divaricatus. Stellaria media* is replaced by *Galium aparine.*

Moisture is usually well retained by Manor soil of woods and there are many species, but because of greater sterility these do not have as luxuriant a growth; the average rate of growth seems to be less.

Castanea dentata was once dominant but has been replaced by *Carya glabra, Liriodendron tulipifera* and *Quercus alba.* The last is most noticeable but not

numerically greater; *Q. rubra* and *Q. velutina* are less frequent while we see *Q. prinus* entering as on the less acid side of its range. *Fagus grandifolia* comes next while *Prunus Mahaleb* is apparently on the acid side of its range. As on Chester soil, *Cornus florida* forms the chief part of the second story, with *Acer rubrum, Sassafras variifolium, Nyssa sylvatica* and *Prunus virginiana* sub-dominate. Facies of the third story are *Benzoin aestivale* and *Viburnum acerifolium; Vitis cordifolia* is still less developed. We see now a true fourth story, of *Vaccinum pennsylvanicum Rhus toxicodendron* and species of *Rubus. Smilax rotundifolia* appears as rather a weak growth. There are many herbs as on Chester loam, and there appear ericads, as *Pyrola americana, Solidago caesia* and *Aster divaricatus* are typical of the late aestival aspect.

Phases of Manor loam found in ravines resemble more closely Chester loam while on exposed hill-slopes the vegetation is quite different, consisting of sparse and often stunted growth of *Quercus prinus, Kalmia latifolia, Rhododendron nudiflorum* and other acid-land plants. This phase has not been considered in the study of Manor loam.

There is a resemblance between this acid hill phase of Manor and the hill-side phase of Dekalb loam; the latter also has phases which are more nearly neutral, in ravines, but vegetation does not make the same amount of growth, the formation is more open, and species are fewer. The soil, being sandy with sandy subsoil, does not retain water; an acid leaf-mold is typical, but aeration is usually good. In ravines we find *Quercus alba* and *Acer rubrum* with sparse *Liriodendron* and *Diospyros virginiana*, and considerable shrub-stratum and herbaceous undergrowth. On gentle hillslopes, considered as typical Dekalb, *Q. alba* is still dominant but *Castanea dentata* was once as numerous; *Q. rubra, Q. velutina* and *Carya glabra* are sparse. Higher, *Populus grandidentata* and more frequently *Betula lenta* occur. There is no great distinction between second and third stories, *Cornus florida* and *Acer rubrum* tending to form shrub-growths while *Amelanchier canadensis* is a small tree. *Nyssa sylvatica* becomes copious in places. A bush-stratum, chiefly ericaceous, occurs while herbs are sparse in scattered families.

The ericads become more numerous as we ascend, notably *Gaylussacia baccata*, while *Smilax rotundifolia* becomes copious. Above, on the exposed summit of the hill-range, there is an open formation of *Quercus prinus*, a shrub stratum of sparce *Kalmia latifolia* and patches of *Epigea repens*, of *Polytrichum* or *Leucobryum*. The soil is decidedly more acid than the type; this phase as well as the ravine have not been included in the tabulated results.

From this soil we pass to Conowingo where in the true type bed-rock comes almost to the surface. On this shallow soil, moist in spring, baked in summer, is found *Nostoc* while the rocks are damp, and fruiting *Cladonias*, while later *Cerastium velutinum, Arabis lyrata* and *Thalinum teretifolium* bloom. Open spaces may be bare in part but are usually covered with *Andropogon scoparius, Paspalum pubescens, Phlox sublata* and *Aster depauperatus*. On the barrens *Pinus virginiana* and *Quercus stellata* replace it.

Conowingo clay has been treated as the type in this paper; it covers a larger area than the barrens. The soil is a light powder when dry, into which water does not penetrate readily; beneath is a stiff clay. Leaves do not decay rapidly and the partly decomposed remains are knit by hyphal strands; mycorhiza are abundant. Fruiting bodies of species of *Clavaria* and of *Fistulina hepatica* are found while on logs are bracket fungi,—not the Myxomycetes and Gasteromycetes of moisture situations, as of Chester loam and ravines of Manor loam.

Plant growth is slow and species are not numerous. *Quercus alba* is dominant with *Fagus* sub-dominant, the trees never reaching a large size. Other trees as *Acer rubrum* and *Nyssa sylvatica* are slender but not clumped. There is practically no shrub stratum, as we found also in dry phases of Hagerstown loam, but plants representing the fourth story of Manor loam are numerous, being ericaceous. In the acid leaf-mold may be found families of *Mitchellia repens*, orchids (*Cypripedium acaule*) and ericads as *Chimaphila maculata*. This undergrowth is less than two feet high and the woods are open. Quadrat surveys for density of species do not give a true idea of the vegetation for some plants are as numerous as on other loams, but are dwarf in size so that the total weight of vegetation per quadrat may be but a third of that on better soils.

CONCLUSIONS

Soil-acidity is one of the ecological factors in plant growth. It apparently has a difference significance for different species, and is possibly never the independently controlling factor. Its exact effect on the plant and the way in which it exerts this effect is still unsettled.

While different soil types, covered by the same (deciduous forest) formation, show different facies, this seems due to a combination of factors, of which available soil moisture is not an inconsiderable one.

SUMMARY

In order to determine the actual soil acidity in a small area throughout the year, with its effect on root distribution and the ecological distribution of wild plants, an intensive study was made of a region about Paoli, Pennsylvania, in Chester County, including five soil types. Borings were made with a soil auger and the samples thus obtained were tested colorimetrically.

Tests showed that the acidity increases to a depth of about 15 cm. after which it decreases, the increase being greatest in the most sterile soils. Soil acidity seems to be correlated with the productiveness of the soil. Monthly tests reveal that there are slight variations from time to time in the soil acidity of a given spot, and that plants growing here cannot be sensitive to small variations in the acidity. Excessive drying, as in drought, was usually accompanied by an increase in acidity, while heavy rains lowered it; acidity was also

increased during freezing. Decay and leaching does not offer a sufficient explanation for the type of curve found, for the same type was found in agricultural soils.

Absorbing roots were found chiefly in the least acid portions of soil, associated with fungi as mycorhiza in the top 15 cm. of the more acid soils, the mycorhiza becoming less abundant in the more nearly alkaline.

Descriptions of consocies of the soil types are given, indicating a correspondence between not only the facies, but the whole flora, and its habitat.

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MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY: VI, NITRIFICATION[1]

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A number of investigators have observed a definite parallelism between the nitrifying capacity and the crop-producing power of the soil, both by the use of the Remy-Löhnis liquid culture method and the fresh soil (or tumbler method). We need call attention only to a few of the outstanding and some of the more recent contributions to this subject.

Löhnis (23) following the work of Remy obtained definite differences in the nitrifying powers of soils bearing upon crop production. A standard solution to which soil extract has been added was used in these studies. Kellerman and Allen (15) demonstrated in 1911 that a close correlation exists between the nitrifying capacity of soils in arid regions and productivity. The relative nitrifying power of very productive soil was found to be 54; of productive soils, 20–36; and of poor soils only 3–5. Greaves (10) found a nearly quantitative relationship between the number of colonies developing on the plate, milligrams of nitric nitrogen formed and nitrogen fixed in cultivated and virgin soils. A correlation between nitrification and soil productivity has also been found by Gutzeit (12), Vogel (29), Brown (3), Noyes and Conner (24), Lipman, C. B. (19), and others, while a close correlation between a high nitrifying power and high productivity has also been observed by Ashby (2), Stevens and Withers (28), Given (9), and Gainey (7). Burgess (4), using the soil method, reported that nitrification is by far the most accurate biological soil test yet perfected for predicting probable fertility. Fischer (5) stated that nitrification can be used for soil characterization. Fraps (6) pointed out that the nitrification test enables one to trace the effect of cropping upon the nitrogen of the soil; ammonia determinations, however, give no increased correlation over the determinations of nitric nitrogen alone. Numerous other observations have been made as to the value of nitrification studies in characterizing soil fertility, including also forest soils. This biological phenomenon can also be used to indicate a distinction between available and unavailable nitrogen, as pointed out by Lipman and Burgess (20, 21).

In some cases, however, the correlation is questioned. Allen and Bonazzi (1), for example, found that the nitrifying capacity of a soil may or may not correlate with its crop producing power, while continuous cropping, especially without fertilization, reduces the nitrifying power of soils. Gerretsen (8) questioned the importance of nitrification as an index of soil fertility, although the two were found to run parallel. The lack of correlation between soil productivity and its nitrifying capacity as reported in some cases may be due merely to the faulty method used in determining the latter.

As pointed out in the previous paper of this series (32), when ammonium sulfate is used for the study of nitrification in soil, especially in the case of acid and poorly buffered soils, the hydrogen-ion concentration resulting from the oxidation of the ammonium salt used in the

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test soon reaches a maximum for the growth and activities of the nitrifying bacteria. Accordingly, when we compare two soils of nearly equal productivity, of which one has received an application of lime while the other has not, the former will show a much higher nitrifying capacity. This difference is due merely to the inadequacy of the common method in which an excess of the ammonium salt is used. This was recognized by Allen and Bonazzi (1), who stated that the customary methods used in studying nitrification are so fraught with errors that we can never hope to solve by them the complex problems encountered. Stevens and Withers (27), for example, reported that 71 per cent of the North Carolina soils do not nitrify. Kellerman and Robinson (17), however, observed a definite correlation between poor nitrification, acid reaction of soil and lack of nodule formation.

When dried blood or other highly concentrated organic nitrogenous substances are used in the nitrification tests, results may again be faulty, particularly in alkaline, poorly buffered soil, due to the large amount of dried blood usually used in the test. The excess of ammonia formed, from the decomposition of the dried blood, in the absence of sufficient buffer or acid substances to neutralize it, will injure greatly the activities of the nitrifying bacteria. Lipman and Burgess (20), for example, found that semi-arid humus-poor soils do not nitrify dried blood which might lead to the conclusion that the use of dried blood as a fertilizer on those soils is inadvisable. Kelley (18) soon pointed out that when, instead of 1 per cent of dried blood, this material is added in low concentrations, the same soil will nitrify it very actively. Kelley concluded, therefore, that results obtained with the use of such high concentrations as 1 and 2 per cent of dried blood or 0.3 and 0.6 per cent of ammonium sulfate, are not a reliable basis for practical conclusions.

Because of the lack of the proper method for studying nitrification, Kelley (18) stated that, "the practical aspects of nitrification studies have become extremely empirical."

The influence of reaction upon nitrification can, therefore, account for a good many results, in which a lack of correlation between nitrification and soil productivity has been recorded. We need but refer here to the work of Wohltmann and associates (34), who found that while the addition of CaO to an acid soil increased its nitrifying capacity (using the soluton method) from 14.1 to 84.7 per cent, the application of manure increased nitrification from 14.1 to 36.1 per cent; $(NH_4)_2SO_4$ to 23.0 per cent; $NaNO_3$, to 31.9 per cent, K_2O and P_2O_5 to 17.8 per cent. The lack of parallelism between nitrification and crop productivity of soils having different reactions particularly when ammonium sulfate is used as the source of nitrogen, is due to the fact that the amount of nitrate formed, under laboratory conditions, is governed by the initial and final soil reactions, as well as presence of bases and buffer content, rather than by the actual nitrifying capacity of the soils, as pointed out elsewhere (32). It is only when the reactions of two or more soils are alike, that nitrification can be compared with soil productivity. Even then we should consider the buffer and base content of the soils.

Stevens and Withers (28) have shown that legumes and stable manure increase the nitrifying efficiency of soils. The favorable influence of manure on nitrification has also been pointed out by Heinze (14), Greaves and Carter (11) and various other investigators. According to Guistiniani (13), nitrification of ammonium sulfate is proportional to moisture content of the soil. Cultivation of soil and addition of organic matter stimulate nitrate formation in soil, as shown by Noyes and associates (25).

Just as in the study of the variability of soil as far as the distribution of numbers of microörganisms are concerned, the variability of the nitrifying capacity of the soil should be considered. Waynick (33) found that the variability of the nitrate content of field samples of soil taken even from an apparently uniform and limited area is high and is of great importance in the estimation of the reliability of any series of results. The variability is still further increased when the samples are treated by the tumbler method for nitrification studies. A single sample was found to be of little value and even a limited number of samples (10 to 16) are subject to wide variations and can give results having only a low degree of accuracy. A composite sample may be considered of value only after the probable error has been determined by the use of a large number of individual samples. Prince (26) compared, at this

laboratory, the variability of the nitrate content and nitrifying capacity of the soil in plots 5A, 7A and 9A, which are described below. Taking twenty-five samples from each plot, he found the coefficient of variability to range between 13 and 42 per cent and the probable error of the mean from 2 to 5 per cent. He found a definite correlation between the crop yields of the three plots with the number of microörganisms and the nitrifying power of the soil.

EXPERIMENTAL

Methods

The following methods were used for the study of nitrification in an attempt to learn whether there is a definite correlation between the nitrifying power of a soil and its crop producing power.

1. Nitrification in pure sand, 100 gm. of pure washed sand and 210 mgm. of $CaCO_3$ were placed in 250 cc. Erlenmeyer flasks and moistened with 10 cc. of distilled water or with a solution containing 1 gm. K_2HPO_4, 0.5 gm. $MgSO_4$ and 0.01 gm. $FeSO_4$ n 1000 cc. of distilled water; the flasks were plugged with cotton and sterilized in the autoclave, at 15 lbs. for 1–2 hours. To each flask were added 5 cc. of a sterile solution of ammonium sulfate equivalent to 30 mgm. of nitrogen. For the inoculation 10 gm. of soil per flask was used. The flasks are then incubated at 27–28°C. for 30 days. This method, just as in the case of the solution methods, is more qualitative than quantitative in nature. The results are apt to be erratic and vary greatly. They are, therefore, more indicative of the activity of the nitrifying flora of the soil than of the nitrate-forming capacity of a given soil itself.

2. Nitrification of soil's own nitrogen. 100-gm. portions of fresh, sieved soil were placed in tumblers, covered with petri dishes and kept at an optimum moisture in the incubator for 30 days.

3. Thirty milligrams of nitrogen as ammonium sulfate per 100 gm. of soil, and treated as 2.

4. Thirty milligrams of nitrogen as ammonium sulfate and 210 mgm. of $CaCO_3$ per 100 gm. of soil. The carbonate is first well mixed with the soil, then the ammonium salt is added. A 21-to 24-day incubation period is sufficient for this test.

5. Dried blood (0.25 gm.) was well mixed in with 100 gm. of fresh sieved soil, kept at optimum moisture in the incubator for 15 days; then the ammonia and nitrate are determined.

As pointed out in the previous paper (32), each one of these methods contributes information necessary for a complete picture of the nitrifying capacity of the soil. This is particularly true of method 4, where the nitrifying capacity of ammonium sulfate is studied in the presence of sufficient $CaCO_3$ to neutralize all the acid formed from the complete nitrification of the ammonium salt.

The nitrates were determined by the phenol-disulfonic acid method. Fifty grams of soil were shaken with 200 cc. of water for about 10–15 minutes in 500-cc. Erlenmeyer flasks, in the presence of a small amount of CaO and filtered through paper. Twenty cubic centimeters of the filtrate were evaporated and treated as usual. The data for nitrification are always given on the basis of milligrams of nitrate nitrogen in 100 gm. of soil.

Soils

The same series of nitrogen plots used in the previous studies (30, 31) were also used for the study of nitrification in the following experiments. The soils were sampled with a borer to a depth of 6.5 inches; 15–25 samples were taken from each plot. The samples were well mixed and sieved through a 3 or 5 mm. sieve. Approximately 60 per cent of the moisture-holding capacity of the soil was used since this was considered an optimum moisture content.

Variability of nitrate content of the soils studied

Plot 9A receiving minerals and 320 pounds of $NaNO_3$ per acre was sampled for the study of nitrate distribution. Fifty-one samples were taken from this plot which is 1/20 of an acre in size. The samples were taken in rows, about equal distance both ways, the outside rows being about three feet from margin of plot. The results are reported in table 1.

TABLE 1

Residual nitrate in soil 9A

SAMPLE NUMBER	NITRATE NITROGEN	DEVIATION FROM MEAN ±	SAMPLE NUMBER	NITRATE NITROGEN	DEVIATION FROM MEAN ±
	mgm.	*mgm.*		*mgm.*	*mgm.*
1	0.65	0.08	29	1.07	0.34
2	1.10	0.37	30	0.21	0.52
3	1.56	0.83	31	0.32	0.41
4	0.92	0.19	32	1.25	0.52
5	0.96	0.23	33	0.33	0.40
6	0.63	0.10	34	1.54	0.81
7	0.86	0.13	35	0.32	0.41
8	0.58	0.15	36	0.27	0.46
9	1.10	0.37	37	0.38	0.35
10	0.65	0.08	38	0.42	0.31
11	1.25	0.52	39	0.45	0.28
12	1.05	0.32	40	0.47	0.26
13	0.42	0.31	41	1.42	0.69
14	0.51	0.22	42	0.86	0.13
15	0.48	0.25	43	0.53	0.20
16	0.60	0.13	44	1.11	0.38
17	0.83	0.10	45	0.35	0.38
18	0.43	0.30	46	0.39	0.34
19	0.46	0.27	47	1.26	0.53
20	0.95	0.22	48	0.75	0.02
21	0.96	0.23	49	0.28	0.45
22	1.28	0.55	50	0.58	0.15
23	0.49	0.24	51	0.17	0.56
24	0.65	0.08			
25	1.02	0.29	Mean	0.73 ± 0.03	0.32
26	0.44	0.29	σ = 0.35 ± 0.02		
27	0.41	0.32	C.V. = 47.9 ± 2.9%		
28	1.08	0.35	Em = 4.5%		

As the average of 61 determinations, the soil in the nitrate-treated plot contains 0.73 mgm. of nitrate nitrogen in 100 gm. of soil or approximately 14.6 pounds per acre. The range is, however, between 1.6 and 30.8 pounds. It is interesting to note that Waynick (33) found by determining the nitrate nitrogen in 100 samples of a California soil 2.70 ± 0.05 mgm. in the surface soil and 0.70 ± 0.03 mgm. in the subsoil, with an average error for the latter of 4.3 per cent. In other words, the amount and variability of the nitrate nitrogen in the plot examined is similar to that found by Waynick in the California sub-soil.

To compare the influence of the period of incubation upon nitrate accumulation in the variously treated soils from organic and inorganic sources of nitrogen, a series of tumblers were prepared using dried blood and ammonium sulfate. At definite intervals, two or three tumblers were taken out for the determination of nitrate, reaction and, in the case of the dried blood, of ammonia. The latter was done with the idea of demonstrating whether the formation of ammonia in the decomposition of the proteins ever becomes a limiting factor to nitrification. A large quantity of the protein source (1 per cent) was used in this experiment so as to have an excess of ammonia present.

As seen in table 2, ammonia formation from dried blood never becomes a limiting factor in the process of nitrification, at least for the soils used in these experiments. Nitrate accumulation depends, however, on the buffer content and the initial reaction of the soil. The results obtained after 15 and after 41 days are distinctly different for the variously treated soils. While the course of nitrate formation was uninterrupted in the case of the manured soils (5A and 5B) and also in the case of the most acid plot (11A), it rapidly came to a stop in the case of the limed and poorly buffered soils. The explanation to that is found in the columns which give the hydrogen-ion concentrations of the soil i.e., the excess of ammonia brought about a rapid increase in the alkalinity of the soil, which completely depressed nitrate formation. It is interesting to note that out of a total of 125 mgm. of nitrogen added to the soil (the dried blood containing 12.5 per cent nitrogen), nearly 121 mgm. were converted into ammonia and nitrate by the most fertile soil (5A); this, of course, includes about 10 mgm. that would have accumulated otherwise in the soil itself.

The results obtained with ammonium sulfate again show that the limiting factor is not the biological flora of the soil, but the initial and final reactions as well as the buffer content of the soil. These phenomena have been considered in detail in the previous paper and need not be dwelt upon here longer.

The soils were sampled five times during the year 1922–1923 and the nitrifying capacity tested by the different methods. The results on nitrate accumulation are given in tables 3–7, while the bacterial numbers for the corresponding dates are reported in table 8. A summary of the treatment, crop yields, bacterial numbers and nitrifying capacity of the various plots are given in table 9.

The results indicate that there is a definite correlation between the nitrifying capacity of a soil and crop productivity, especially in soils not modified by the application of lime. The nitrifying capacity of the soil depends on the physical, chemical and biological conditions of the soil, the most important of the physical and chemical factors being the buffering properties of the soil, hydrogen-ion concentration, presence of lime and perhaps of soluble phosphates and other minerals. The number and efficiency of the organisms oxidizing ammonia to nitrates, as well as the amount of nitrate removed by soil fungi and bacteria, account for the biological efficiency of a soil to accumulate

TABLE 2

Course of nitrate formation from dried blood and ammonium sulfate in variously treated soils, May 22, 1922

PLOT NUMBER	DRIED BLOOD* (1 PER CENT)												AMMONIUM SULFATE (30 MGM. OF N IN 100 GM. OF SOIL)							
	NH_3-N in 100 gm. soil after:		NO_3-N in 100 gm. soil					Reaction after					NO_3-N in 100 gm. soil after:				Reaction after			
	7 days	41 days	3 days	7 days	15 days	27 days	41 days	0 days	3 days	7 days	15 days	27 days	7 days	15 days	27 days	41 days	7 days	15 days	27 days	41 days
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*pH*	*pH*	*pH*	*pH*	*pH*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*pH*	*pH*	*pH*	*pH*
5 A	45.2	64.9	5.6	6.0	13.8	42.2	56.0	5.4	6.2	7.1	7.4	5.8	0.7	1.8	4.3	5.9	5.4	5.2	5.0	4.7
7 A	38.1	72.8	3.4	2.7	3.1	4.8	4.4	4.8	6.2	7.0	7.6	8.1	0.13	0.2	0.56	0.40	4.8	...	4.4	4.4
9 A	34.0	76.2	5.1	4.1	6.7	7.6	7.6	5.8	6.4	7.3	7.8	8.2	0.7	2.2	4.8	4.4	5.4	...	4.6	4.6
11 A	44.2	87.8	3.1	2.1	3.5	5.0	15.2	4.6	6.6	7.0	7.6	7.9	0.3	0.4	0.5	0.4	4.4	...	4.2	4.2
19 A	39.3	82.6	4.9	3.0	3.8	8.8	4.6	5.4	6.4	7.2	7.8	8.0	0.2	0.5	1.6	1.7	5.2	4.9	4.4	4.4
5 B	42.0	45.5	9.1	10.2	17.0	43.2	52.0	6.4	7.6	8.0	7.5	6.8	2.4	5.6	12.4	16.1	5.6	5.2	4.6	4.4
7 B	40.1	49.8	5.0	3.4	4.4	5.4	4.6	6.2	7.8	9.0	8.8	8.4	0.5	2.5	7.2	9.4	5.3	...	4.6	4.4
11 B	47.5	59.5	3.4	3.2	3.4	4.9	5.2	5.7	7.1	8.5	8.6	8.6	0.4	0.9	3.8	4.9	5.4	...	4.6	4.4

* By nitrates, we must understand all substances giving the characteristic reaction with phenol-disulfonic acid. The dried blood, for example, used in our studies was found to contain about 3 mgm. of nitrate-nitrogen in 1 gm. of dried blood, as determined by the phenol-disulfonic acid method.

TABLE 3

Nitrification of ammonium sulfate in sand plus $CaCO_3$

PLOT NUMBER	JULY 10, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	*mgm.*	*mgm.*	*mgm.*
5 A	2.80	1.35	0.72	1.62
7 A	0.21	0.14	0.09	0.14
9 A	....	0.68	0.20	0.44
11 A	0.44	0.40	0.12	0.32
19 A	....	0.22	0.15	0.19
5 B	....	4.30	0.65	2.48
7 B	0.94	0.21	0.51	0.55
11 B	2.20	1.30	0.26	1.25
19 B	....	0.56	0.30	0.43

TABLE 4

Nitrification of soil's own nitrogen

PLOT NUMBER	JULY 10, 1922	AUG. 17, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5 A	2.50	1.24	0.98	2.30	1.76
7 A	0.38	0.48	0.52	0.70	0.52
9 A	....	0.84	0.74	1.25	0.94
11 A	0.84	0.52	0.78	1.05	0.80
19 A	....	0.76	0.74	1.05	0.85
5 B	....	....	0.72	1.90	1.31
7 B	0.60	0.58	0.26	0.75	0.55
11 B	0.94	0.22	0.58	0.90	0.66
19 B	....	0.96	0.48	1.30	0.91

TABLE 5

*Nitrification of ammonium sulfate in soil**

PLOT NUMBER	MAY 22, 1922*	JULY 10, 1922*	AUG. 17, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5 A	4.30	5.20	3.90	3.90	3.80	4.22
7 A	0.56	0.38	0.37	0.41	0.50	0.44
9 A	4.80	4.90	3.10	3.30	3.60	3.90
11 A	0.50	0.76	0.49	0.53	0.30	0.52
19 A	1.60	1.72	0.94	0.82	1.20	1.26
5 B	12.40	11.60	10.70	7.80	7.20	9.94
7 B	7.20	6.20	8.60	4.10	4.10	6.04
11 B	3.80	3.80	6.10	2.90	2.90	3.90
19 B	10.40	8.90	9.20	5.00	5.20	7.74

* Incubation period for samples taken May 22 and July 10 was 30 days; for the rest, only 25 days.

TABLE 6

Nitrification of ammonium sulfate, in presence of a theoretical amount of $CaCO_3$

PLOT NUMBER	JULY 10, 1922*	AUG. 17, 1922	AUG. 30, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5 A	24.40	33.40	30.40	17.40	23.20	25.76
7 A	7.60	7.10	5.20	4.30	6.80	6.20
9 A	22.10	23.20	19.60	13.70	19.60	19.64
11 A	3.10	11.40	4.40	6.90	7.80	6.72
19 A	7.90	11.80	6.60	6.50	9.90	8.54
5 B	30.90	30.80	29.60	23.30	29.40	28.80
7 B	16.95	26.10	25.80	15.20	20.20	20.85
11 B	26.60	32.20	22.60	19.30	25.30	25.20
19 B	24.20	28.60	29.60	19.60	26.30	25.66

* 50 mgm. of nitrogen used in this case.

TABLE 7

Nitrification of dried blood (0.25%) in the soil

PLOT NUMBER	JULY 10, 1922*	AUG. 17, 1922	AUG. 30, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
5 A	24.40	10.20	7.60	6.40	6.10	10.94
7 A	7.20	2.40	2.00	2.30	1.60	3.10
9 A	17.20	6.00	7.40	5.30	5.10	8.20
11 A	5.00	2.20	1.20	2.40	1.50	2.46
19 A	8.60	2.80	2.40	3.10	2.50	3.88
5 B	25.30	19.20	15.00	15.10	14.60	17.84
7 B	18.30	13.60	8.40	9.40	7.10	11.36
11 B	21.20	15.40	11.60	10.60	5.00	12.76
19 B	20.10	17.00	10.80	8.90	10.70	13.50

* Incubation period 25 days for July 10 sampling and 13–15 days for the other dates.

TABLE 8

Numbers of microörganisms in the soil (thousands per gram)

PLOT NUMBER	JULY 10, 1922	AUG. 17, 1922	AUG. 30, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
5 A	16,660	8,890	14,500	15,540	14,000	13,920
7 A	6,180	5,430	6,800	3,000	5,300	5,342
9 A*	.....	10,600	13,250	8,800	11,700	11,088
11 A	5,540	7,600	5,100	5,100	4,400	5,548
19 A	.....	6,770	9,440	4,800	7,900	7,228
5 B	13,560	8,410	11,600	10,800	14,600	11,794
7 B	8,600	8,110	7,200	6,500	9,900	8,062
11 B	10,700	9,260	8,350	6,600	9,500	8,882
19 B	.....	9,500	9,600	7,700	12,000	9,700

* Attention should be called here to an unpardonable error that has crept into the graph of the third paper of this series (30) where 9B should read 9A.

TABLE 9

Chemical and biological condition of soil and crop productivity

PLOT NUMBER	NITROGEN CONTENT*	CARBON CONTENT*	NITROGEN APPLIED PER ACRE IN 14 YEARS	NITROGEN RECOVERED IN CROP IN 14 YEARS	CROP YIELD PER ACRE		REACTION	BACTERIAL NUMBERS		NITRIFYING CAPACITY		TREATMENT
					15 years	1922		Per gram	Comparative basis	NO_3-N per 100 gm. soil‡	Comparative basis	
	per cent	*per cent*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*pH*	*millions*		*mgm.*		
5 A	0.1463	1.73	2519	690	69,500	5600	5.5	13.9	262	8.86	450	Minerals§ and 16 tons of cow manure
7 A	0.0826	0.96	0	164	15,464	328	5.0	5.3	100	2.08	100	No fertilizer
9 A	0.0994	1.17	693	557	57,968	4480	5.8	11.1	210	6.62	318	Minerals and 320 lbs. $NaNO_3$
11 A	0.1064	1.23	693	497	41,754	180†	4.6	5.5	104	2.16	104	Minerals and $(NH_4)_2SO_4$ equivalent to 320 lbs. $NaNO_3$
19 A	0.1008	1.13	0	294	29,926	660	5.4	7.2	136	2.82	135	Minerals only
5 B‖	0.1428	1.74	2519	606	59,754	4720	6.4	11.8	223	12.07	580	Minerals, manure, and lime‖
7 B	0.0868	1.18	0	312	30,160	960	6.3	8.0	151	7.87	378	Lime only
11 B	0.0952	1.10	693	635	61,906	4680	5.8	8.9	168	8.75	440	Minerals, $(NH_4)_2SO_4$ and lime
19 B	0.0924	1.18	0	341	35,930	2400	6.4	8.7	183	9.65	464	Minerals and lime

* The total carbon and nitrogen in this summary differ from those given in a previous paper, the former being determined this year in this laboratory, while the latter was taken from the paper of Lipman and Blair (22).

† Also 1100 pounds *Rumex acetosella*.

‡ Average of the five different tests.

§ Minerals = 640 pounds acid phosphate and 320 pounds of potassium chloride per acre.

‖ B plots received per acre 1 ton of lime in 1908; 2 tons, in 1913; and 2 tons, in 1918.

nitrates. It is important to note that here again, even more than in the case of numbers, the addition of lime to the soil brought about a greater stimulus to the nitrifying efficiency of the soil than in crop productivity. This is due chiefly to our methods of studying nitrification, whereby amounts of nitrogen sources are added to the soil much in excess of what would be used under field conditions. Under these artificial conditions, where acids are formed from the oxidation of the ammonium salt by organisms which are rather sensitive to an excess of acid, it is but natural to expect that the addition of lime to the soil will favor the process of nitrification in the laboratory, independent of

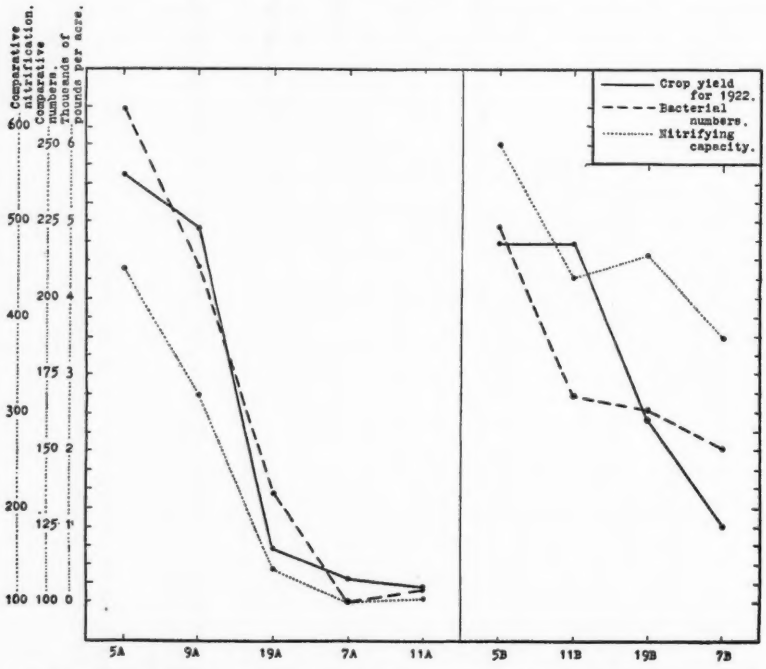

FIG. 1. INFLUENCE OF SOIL FERTILIZATION UPON CROP YIELD, NUMBERS OF MICROÖRGANISMS DEVELOPING ON THE PLATE AND NITRIFYING CAPACITY OF THE SOIL

its actual effects under field conditions. It is sufficient to inspect table 4 to find that no more nitrate will accumulate in the soil, without any addition of an excess amount of nitrogen, in the limed than in the unlimed soils. We can expect a more accurate correlation and the elimination of the disturbing influence of liming of soil only after we have developed our methods to an extent as to have laboratory conditions absolutely comparable with phenomena taking place in the field.

The graphs in figure 1 show conclusively that there is a correlation between the crop productivity of the soil on the one hand and numbers of microörgan-

isms and nitrifying capacity of the soil on the other, allowing for the disturbing influence of liming of an acid soil. The fertility of a soil is affected not only by its biological phenomena but also by its physical and chemical conditions, especially by the amount of fertilizing elements present in the soil or added previous to, or during the process of growth, as well as by the kind of crop grown. We cannot expect, therefore, that the results of a biological study of soil, especially if not all activities are concerned and properly interpreted, should give an exact mathematical interpretation of the productive capacity of the soil. It is sufficient to point out the parallelism. This combined with our knowledge of the physical and chemical nature of the soil can explain the productivity of the soil.

SUMMARY

In the study of soil microbiological methods as a possible means of measuring the present and future crop-producing power of soils, certain relations and tendencies are clearly indicated. Soil microbiological research has not yet gone far enough to justify our using any soil microbiological factor as an index of soil productivity. Nevertheless, the author feels justified in pointing out that the data submitted in the present paper together with those published previously bring out certain correlations, which may help in time to place in our hands quantitative as well as qualitative methods for measuring the productive power of soils.

The results presented in this paper on the nitrifying power of the soil indicate that nitrification studies can yield information for the differentiation of soil fertility just as well as the study of numbers of microörganisms in the soil. Liming of the soil stimulates the nitrifying capacity of the soil and affects, therefore, the parallelism between the results obtained in the laboratory from the study of nitrification and crop yields. However, since soil fertility is affected, aside from the biological activities of the soil, also by its physical and chemical conditions, the results should not be expected to be a mathematical function of crop productivity of a given soil.

It is necessary to add here a further word of caution, so as to prevent any misunderstandings that might have arisen from the studies reported in these papers. The results of the investigations thus far reported indicate that a study of numbers of microörganisms in the soil and of nitrification yield results which can be used as indices of soil fertility; it is questionable whether ammonia formation in either soil or solution can be used for that purpose. It is important to keep in mind that these studies have been carried out with one soil type (Sassafras gravely loam), slightly acid in reaction (uncultivated, about pH = 6.0 to 6.2), divided into a group of plots which have been fertilized alike for a number of years. The differences thus established are due to differences in treatment. It remains to be seen whether the same results will be obtained when various soil types are employed.

The writer is indebted to Mr. R. L. Starkey for aid in taking the samples; to Miss C. Wark for assistance in the laboratory determinations; to Dr. J. G. Lipman and Prof. A. W. Blair for permission to use the soil plots and data on crop yields; and to Dr. J. Lipman for reading the manuscript.

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INFLUENCE OF SOIL MOISTURE AND ACIDITY ON THE DEVELOPMENT OF POTATO SCAB[1]

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In a recent paper Sanford (1) indicates that soil reaction may not be the most important factor in influencing the development of common scab of potatoes. He shows that with an increase in soil moisture content there was a decrease in the amount of infection on the tubers and as a result of hydrogen-ion determinations made of the soils of various moisture content, he found that the dry soils were slightly more acid than the moist soils and concludes that moisture and not acidity was the controlling factor. The differences in the pH values of the dry and moist soils were very slight, however, and in every case the values indicated were within the limiting range for the best development of *Actinomyces scabies*.

As the result of a series of potato scab control and infection studies conducted during the past three years at the New Jersey Agricultural Experiment Stations, considerable data has been accumulated on the relation of the scab organism to soil conditions. The weather conditions, especially rainfall, have been widely different in these three years. In 1920 the rainfall was well above the average and in 1922 slightly above the average, while in 1921 it was below average. In 1920 the mean rainfall for the state for the months of April to September inclusive, was 29.21 inches, for the same months in 1921 and 1922, 21.26 inches and 24.78 inches respectively. The 34-year average for these months was 24.4 inches. In 1921 there were only 6.85 inches of rain in the months of June and July as compared with 11.94 and 12.10 for the corresponding months in 1920 and 1922. The temperatures for these periods were not far different, the mean for the state for the months of June to September inclusive was 69.8°F. in 1920 and 71.7° and 70.5° for the same months for 1921 and 1922.

A series of field tests started in 1920 was continued in 1921 and 1922 to determine the residual effect of sulfur applications on both the yield of potatoes and the control of scab. The soil on which these tests were conducted is a sassafras loam which in 1919 had grown a crop of potatoes so scabby as to be almost entirely unsalable. A section of this field was divided into eightieth-

[1] Paper No. 132 of the Journal Series New Jersey Agricultural Experiment Stations Department of Plant Pathology.

acre plots. In every case the sulfur applications were made just before the crop was planted. Soil samples were taken in the spring and fall of each year and their hydrogen-ion concentration determined. The results of one of these tests is presented in table 1. The figures given in the table represent the average of six untreated and three sulfured plots.

From the table it will be seen that the yield in 1921 on both the treated and check plots was greatly reduced as compared with that of 1920 and 1922. This decrease was the result of the dry season.

It will be observed likewise that scab was much more severe in this than in the other two years. In this connection it is interesting to note that on the untreated plots the number of unsalable tubers increased with a decreased rainfall. In 1920, 76.3 per cent of the crop was unsalable as compared with 87.2 and 99.3 per cent in 1922 and 1921. It will be recalled that the rainfall for the summer months in these three years was 29.21, 24.78 and 21.26 inches respectively. This is in entire accord with Sanford's conclusion that soil

TABLE 1

Relation of rainfall and soil acidity to the development of potato scab

YEAR	TREATMENT	RAINFALL APRIL–SEPTEMBER	YIELD PER ACRE	CLEAN TUBERS	SALABLE TUBERS	UNSALABLE TUBERS	REACTION
		in.	*bu.*	*per cent*	*per cent*	*per cent*	*pH*
1920	Check	29.21	238.1	1.6	22.2	76.3	6.8
1921	Check	21.26	77.0	0.0	0.7	99.3	6.4
1922	Check	24.78	230.7	0.0	12.5	87.2	6.7
1920	600 lbs. inoculated sulfur		226.2	64.7	25.7	9.5	4.8
1921	300 lbs. inoculated sulfur		77.6	10.4	48.9	40.7	4.8
1922	600 lbs. inoculated sulfur		250.6	79.4	19.1	1.5	4.2

moisture is an important factor in determining the severity of scab. These differences in the amount of scab were apparent despite the fact that, in the case of the check plots, the mean hydrogen-ion exponent values were slightly lower in 1921 than in the other two years, and on the sulfur plots the mean values in 1920 and 1921 were identical.

A consideration of the hydrogen-ion concentration values of the soils from treated and untreated plots indicates, however, that soil moisture is by no means the only contributory factor. In 1921 the mean pH value of the check plots was 6.4 and on these 99.3 per cent of the crop was unsalable. On the other hand, on the sulfur plots, with a pH value of 4.8, only 40.7 per cent of the tubers were unsalable. This difference, amounting to 58.6 per cent in the number of unsalable tubers must be attributed to the differences in acidity since, as these plots were adjoining, it may be assumed that there was little variation in soil moisture content. The same relation holds for 1920 and 1922. In these two years still greater decreases were recorded in the number of unsalable tubers on the treated as compared with the untreated plots.

The relation of soil acidity and moisture to scab infection is still further apparent from a consideration of the data from the sulfur plots in 1920 and 1922. In the former year 64.7 per cent of the crop was free from scab as compared with 79.4 per cent in 1922. In this case the recorded differences in the number of clean potatoes cannot be attributed to any difference in soil moisture content since in 1920 the rainfall in the summer months was 4.43 inches greater than in 1922.

From table 1 it will be observed that the pH values of these plots was 4.8 in 1920 and 4.2 in 1922. In this instance the decrease in the number of scabby tubers must be attributed to an increase in soil acidity and not to a lessened soil moisture content.

In a second test conducted in this same field, a similar relation was found to exist between acidity and scab infection. The results of this test are presented in table 2, the figures given representing averages of 6 check and 3 treated plots.

TABLE 2

Influence of rainfall and soil acidity on the development of potato scab

YEAR	TREATMENT	RAINFALL APRIL–SEPTEMBER	YIELD PER ACRE	CLEAN TUBERS	SALABLE TUBERS	UNSALABLE TUBERS	REACTION
		in.	*bu.*	*per cent*	*per cent*	*per cent*	*pH*
1920	Check	29.21	209.1	15.2	28.0	51.0	6.7
1921	Check	21.26	127.6	0.0	4.4	95.6	6.6
1922	Check	24.78	317.9	4.4	34.2	61.4	6.4
1920	300 lbs. inoculated sulfur		325.0	37.2	35.3	27.5	6.0
1921	300 lbs. inoculated sulfur		107.7	10.9	53.5	35.6	4.8
1922	600 lbs. inoculated sulfur		292.4	72.0	23.3	4.7	4.6

From the table it will be seen that here again scab was much more severe on both the treated and untreated plots in 1921 than in 1920 or 1922. On the plots treated with sulfur, 35.6 per cent of the crop was unsalable in 1921 and only 27.5 per cent in 1920, although the mean pH values were 4.8 in the former and 6.0 in the latter year. It is evident that soil moisture is a limiting factor in determining the amount of scab, but with the same moisture content the disease is very much reduced by increasing the soil acidity as is apparent from the fact that in 1921, on the sulfur plots, with a pH value of 4.8, the crop was 35.6 per cent unsalable, while on the check plots, with a pH value of 6.6, 95.6 per cent of the crop was unsalable.

In this test, as in the one previously discussed there was considerably less scab in 1922 than in 1920 on the plots treated with sulfur. In the former year, with a pH value of 6.0 only 37.2 per cent of the crop was clean, while in 1922, the pH value of these plots was reduced to 4.6 with a corresponding reduction in the number of scabby tubers, 72.0 per cent of the crop being clean.

GREENHOUSE EXPERIMENT, 1921–1922

In order to obtain more definite information on the question, an experiment was conducted in the greenhouse in the winter of 1921–1922 to determine the influence of soil moisture on the amount of scab and also its influence on the oxidation of sulfur. The soil used in this test was a sassafras loam taken from the field in which the tests previously discussed were conducted. Two series of 2-gallon jars were run, each consisting of 12 cultures, allowing for 4 replications of each of the moisture contents employed. On the basis of water-holding capacity, the per cent moisture contents of the various cultures were 30, 40, 50, 60, 70 and 80. The cultures in one of the series were run as checks while in the other series each culture received an application of sulfur at the rate of 900 pounds per acre. In addition, a 4–8–5 fertilizer mixture was added to all the cultures at the rate of 1500 pounds per acre. Each culture was weighed at frequent intervals during the progress of the experiment and the water lost through evaporation and transpiration replaced. The soil in the cultures made up to 70 and 80 per cent of the water-holding capacity was so wet that the seed pieces rotted and no readings were obtained.

In order to obtain vigorous plants in all of the cultures, twelve tubers of the Irish Cobbler variety were selected in the fall of 1921 from plants that were free from disease. The tubers were disinfected for 1.5 hours in a solution of 1–1000 mercuric chloride. Each of the tubers was then cut into two pieces weighing 41 gm. each and including three eyes; one of these pieces was planted in a culture treated with sulfur and the other in its check of the same moisture content. Soil samples were taken from each culture at time of planting and again at approximately 10-day intervals until the experiment was concluded; hydrogen-ion determinations were made by the colorimetric method at the time of sampling.

The experiment was started on November 18, 1921, and concluded February 24, 1922. Soil temperature readings were taken at 3-day intervals during the progress of the experiment. While the temperature in the low moisture cultures was higher than in those of high moisture content, the range was very small, the mean values being 24.38°C. and 23.95°C. respectively. At time of harvesting, the green weights of the tubers, the number of tubers showing scab, and the per cent of the surface of each that was scabbed was obtained. The results are presented in table 3. This table is divided into two sections. In section 1 is given the results from the check, and in section 2 the sulfur series. From the first column of section 1 it will be seen that with an increase in the soil moisture content, there was a marked increase in the weight of tubers harvested, while in the second column it will be seen that all of the tubers, regardless of soil moisture content, showed scab. It will be observed, however, that with each increase in soil moisture content, there was a decrease in the per cent of surface scabbed; in the cultures with highest moisture content, 38.5 per cent of the surface was scabbed as compared with 84.7 per cent in the culture with lowest moisture content.

In the series treated with sulfur, there was a marked decrease in the number of tubers showing scab as well as in the per cent of surface scabbed. In the cultures of low moisture content, 41 per cent of the surface of the tubers was scabbed as compared with 2.5 per cent of the surface of the tubers produced in the cultures of high moisture content. It is apparent that in this experiment, as in the field tests, soil moisture was a factor of considerable importance in determining the amount of scab; that this is not the only or the most important factor, however, is clear from a consideration of the pH values of these two series. The initial pH value of the soils in each culture in both series was 6.9. In the series receiving no sulfur, only slight differences were observed during the progress of the experiment, regardless of soil moisture content. On the other hand, in the sulfur series, at the time the second soil samples were taken, ten days after the sulfur application was made, the pH values decreased to 6.4. Similar decreases were observed on subsequent sampling until at the time the plants were harvested; the exponent value of the cultures with 30 to 60 per cent moisture content was uniformly 5.1.

TABLE 3

Influence of soil moisture and acidity on the development of potato scab

SOIL MOISTURE WATER-HOLDING CAPACITY	NO-SULFUR SERIES				SULFUR SERIES			
	Weight of tubers	Scabby tubers	Amount of surface scabbed	Reaction	Weight of tubers	Scabby tubers	Amount of surface scabbed	Reaction
per cent	*gm.*	*per cent*	*per cent*	*pH*	*gm.*	*per cent*	*per cent*	*pH*
30	38.0	100	84.7	6.8	33.35	100	41.0	5.1
40	69.9	100	82.3	6.9	51.15	66.6	9.7	5.1
50	68.1	100	75.8	6.9	62.7	83.3	6.6	5.1
60	68.7	100	38.5	6.9	46.7	55.5	2.6	5.1

A comparison of sections one and two of table 3 shows that in every instance, regardless of soil moisture content, there was considerably less scab in the cultures with low than in those with high pH values. In those with the moisture content adjusted to 30 per cent of their water-holding capacity and with a pH value of 5.1, only 41.0 per cent of the surface was scabbed as compared with 84.7 per cent in the cultures with a pH value of 6.8. In the check cultures with highest moisture content, all of the tubers were infected with 38.5 per cent of the surface scabbed while in the cultures receiving sulfur only 55.5 per cent of the tubers were infected and these showed only 2.6 per cent of the surface scabbed. The mean pH values of these cultures was 6.9 and 5.1 respectively. In the light of these results it is evident that while soil moisture is an important factor in determining the amount of scab, soil acidity is of equal and probably of greater importance since with the same moisture content scab is less severe on soils with an acid than on those with an alkaline reaction.

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A MODIFICATION OF THE TRUOG SOIL ACIDITY TEST[1]

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The Truog soil acidity test (3) is widely used as a practical test for soil acidity but has had a limited use in research work. This is probably due to the fact that the test is not sufficiently quantitative for research purposes. It is difficult to detect small differences in acidity, especially among strongly acid soils, and more difficult to satisfactorily record the results. Despite these objections the method has given results that compare favorably with other methods (1), (2) and the authors have found the method useful for certain lines of work. In using the test as a means of indicating changes in acidity due to different soil treatments, it seemed desirable to modify it in such a manner as to overcome the two objections mentioned above. The modification as described in this paper makes possible a more accurate quantitative expression of the results of the test and affords a simple, rapid and accurate method of determining differences in soil acidity.

In the modified test the amount of hydrogen sulfide evolved on boiling the soil with Truog's reagent is accurately determined by titration with a standard solution of iodine instead of permitting it to react with a lead acetate paper. In order to secure a larger amount of hydrogen sulfide for the determination, the amount of soil used in making the test has been increased from ten to twenty grams and the time of boiling increased from two to three minutes. The procedure developed for making the modified test is as follows:

Weigh out 20 gm. of air-dry soil and place it in a 500 cc. Erlenmeyer flask, add 100 cc. of a one per cent solution of $BaCl_2$ containing, in suspension, 0.10 gm. of neutral ZnS. Place the flask on a wire gauze over a bunsen burner and connect with a 6-mm. glass delivery tube. The delivery tube is twice bent at right angles to form two parallel arms 10 cm. apart. The short arm is 5 cm. long and passes through a rubber stopper into the Erlenmeyer flask. The other arm is 41 cm. long and extends to within 3 cm. of the desk or when finally placed in position to within 1 cm. of the bottom of a 50-cc. graduated cylinder. After the contents of the flask have come to a boil and as soon as steam has been emitted from the long arm of the delivery tube for 10 seconds, the flask is raised and the delivery tube inserted into a 50-cc. graduated cylinder containing exactly 25 cc. of 4 per cent solution of NH_4OH. The cylinder must be in a bath of cold water which prevents the contents being raised to the boiling point. Boiling is continued for 3 minutes, after which the delivery tube is removed from the cylinder. The flame of the burner must be adjusted so that just 10 cc. of water will be distilled over in the 3 minutes of boiling. Remove the cylinder from the beaker, read and

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record the increase in volume which should be 10 cc. Transfer the solution to a 100-cc. beaker, add 10 cc. of 0.01 *N* iodine and 2 cc. of a freshly prepared starch indicator solution, acidify with 2 cc. of concentrated HCl. The excess of iodine is now titrated with 0.01 *N* $Na_2S_2O_3$ and the amount of H_2S evolved is calculated. One cubic centimeter of 0.01 *N* iodine is equivalent to 0.17 mgm. H_2S. Duplicate determinations should agree to within 0.02 mgm. H_2S.

EXPERIMENTAL

When using the quantities of soil and reagent recommended by Truog, the amount of hydrogen sulfide evolved during two minutes of boiling is so small in the case of slightly acid soils that it is apparent that the accuracy of the determination can be increase by modifying the test so that larger quantities of hydrogen sulfide are evolved. The following experimental results show the effect of varying amounts of soil, reagent and time of boiling on the amount of hydrogen sulfide secured in the determination.

Table 1 gives the amount of hydrogen sulfide evolved when different quantities of soil were used in making the test. In all instances 1.1 gm. of the re-

TABLE 1

Hydrogen sulfide evolved in the modified Truog test when varying quantities of soil were used

AMOUNT OF SOIL USED	SOIL NO. 41		SOIL NO. 44	
	H_2S	H_2S	H_2S	H_2S
gm.	*mgm.*	*relative amount*	*mgm.*	*relative amount*
5	0.433	100	0.148	100
10	0.773	178	0.292	197
20	1.292	298	0.462	312
30	1.530	353	0.581	392

agent was used and boiling continued for three minutes at such a rate that 10 cc. of water was distilled over. The results are the averages of closely agreeing duplicates. According to the Truog test, soil 41 is very strongly acid and soil 44 is medium in acidity.

The results show that the evolution of hydrogen sulfide is greatly increased by increasing the quantity of soil. Twenty grams of soil was taken as a convenient amount to use in the modified test. Increasing the quantity of soil above 20 gm. did not greatly increase the amount of hydrogen sulfide evolved and the larger quantity increased frothing when boiling started.

Table 2 gives the amount of hydrogen sulfide evolved when different quantities of reagent were used in making the test. In these determinations 20 gm. of soil were used and boiling was for three minutes.

Increasing the quantity of reagent above 1.1 gm. the quantity recommended by Truog decreased the amount of hydrogen sulfide secured from the strongly acid soil and caused only a very small increased production from soil 44. This indicates that 1.1 gm. of the reagent, containing 1 gm. of barium chloride and 0.1 gm. of zinc sulfide, is the best quantity of the reagent to use in the

test. This quantity is accurately secured by taking 100 cc. of a 1 per cent solution of barium chloride containing, in suspension, 1 gm. of neutral zinc sulfide per liter. The suspension must be thoroughly shaken each time before measuring out the 100 cc.

The amount of hydrogen sulfide secured for a determination may be increased by absorbing the hydrogen sulfide evolved during a longer period of boiling than the two minutes recommended by Truog. However, prolonged boiling may be objectionable due to side reactions and alterations in the acidity of the soil. The influence of time of boiling on the quantity of hydrogen sulfide produced is shown in table 3. Twenty grams of soil and 1.1 gm.

TABLE 2

Hydrogen sulfide evolved in the modified Truog test when varying amounts of reagent were used

AMOUNT OF REAGENT USED	SOIL NO. 45		SOIL NO. 44	
	H_2S	H_2S	H_2S	H_2S
gm.	*mgm.*	*relative amount*	*mgm.*	*relative amount*
0.55	1.278	100	0.374	100
1.1	1.351	105.7	0.462	123.5
2.2	1.249	97.7	0.476	127.2
3.3	0.909	71.1	0.479	128.0

TABLE 3

Hydrogen sulfide evolved in the modified Truog Test during successive one-minute intervals

PERIOD OF BOILING	SOIL NO. 41		SOIL NO. 44	
	H_2S	H_2S	H_2S	H_2S
min.	*mgm.*	*relative amount*	*mgm.*	*relative amount*
1	0.4992	100.0	0.1907	100.0
2	0.4207	84.2	0.1496	78.4
3	0.3496	70.0	0.1252	65.6
4	0.3029	60.6	0.1122	58.8
5	0.2898	58.0	0.1028	53.9
6	0.2337	46.8	.....	.....

of reagent were used. The hydrogen sulfide evolved during successive 1-minute periods was determined. The results show that more hydrogen sulfide is evolved during the first 1-minute period than during any succeeding minute. The quantity evolved decreases with each successive period, the decrease being most marked in the second period. The relative decrease was very nearly the same for the two soils as can be seen from an inspection of the figures in the third and fifth columns of table 3. Three minutes is considered the most desirable length of time for boiling since it gives more hydrogen sulfide for the determination, is not long enough to permit side reactions to seriously interfere with the test, and during that time a convenient volume of water is distilled over.

Fifty soils have been tested by both the regular and modified Truog tests. The results of the two tests agree closely, as would be expected. When the soils were arranged in the order of their acidity they were placed in approximately the same order regardless of the method used. However, the modified test permitted a much better comparison and made evident differences that could not be detected with the test paper. For instance, the test papers for soils 15 and 4 appeared to be identical but according to the modified test 1.191 mgm. of hydrogen sulfide was evolved from soil 15 while 1.352 mgm. was evolved from soil 4. The test papers from soils 12, 24, 13 and 5 appeared identical, but the quantities of hydrogen sulfide evolved were 0.691, 0.700, 0.725 and 0.802 mgm. respectively. In general, with soils of slight and medium acidity, it is difficult to detect with the regular test differences in acidity corresponding to 0.075 or 0.100 mgm. of hydrogen sulfide as indicated by the modified test. If the soils are strong or very strong in acidity the test papers may not show differences corresponding to 0.200 to 0.300 mgm. of hydrogen sulfide. These results show that when the acidity of a number of soils is being compared, as has been done by Johnson (1) and Parker and Bryan (2), the modified test would be very useful.

SUMMARY

1. A modification of the Truog soil acidity test is proposed for use in research work.

2. The suggested modification consists of absorbing the hydrogen sulfide evolved in the test in dilute ammonia. An excess of standard iodine solution is then added, the solution acidified and the excess iodine is titrated with standard sodium thiosulfate of the same normality. The results of the test are recorded as milligrams of hydrogen sulfide evolved.

3. Increasing the quantity of soil used in making the test increases the amount of hydrogen sulfide evolved. Increasing the quantity of reagent above 1.1 gm. does not increase and may decrease the amount of hydrogen sulfide evolved.

4. The modified test affords a short, simple and accurate method of determining slight differences in soil acidity.

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A COMPARISON OF THE JONES CALCIUM ACETATE METHOD FOR LIME REQUIREMENT WITH THE HYDROGEN-ION CONCENTRATION OF SOME QUEBEC SOILS

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The problem of soil acidity is one that is common to most soils of humid regions. A large amount of investigation has been carried on to determine the nature of the phenomenon and to find a satisfactory method for its determination. The methods that have been advanced are many and vary greatly in principle and technique. These have been studied from time to time in relation to one another, and in relation to field conditions with the idea of selecting the most satisfactory, if any. MacIntire (15) has reviewed and cited the most important literature on the subject.

Lime requirement methods are intended to measure the total amount of base necessary to neutralize a soil; that is, to change the reaction to pH 7. Whether a particular method accomplishes this can only be determined by a consideration of the hydrogen-ion concentration. There are two means by which the hydrogen-ion concentration of a soil may be determined, viz; directly with the hydrogen electrode, and indirectly by the comparison of the color of the appropriate indicator in a standard solution with that of the same indicator in the aqueous extract of the soil. The former is more accurate, while the latter is simpler. Gillespie (6) was the first investigator to report comparisons of the two methods and he has shown fair agreement. Since that time one or the other of these procedures has been used by different workers in soil studies and for the investigation of lime requirement methods. Knight (13) studied a series of soils, the lime requirement of which had been previously determined by several different methods and determined their hydrogen-ion concentration with the hydrogen electrode. He used a type of electrode, however, which required the use of a neutral salt solution, so that his results are not comparable with others. Blair and Prince (1) and Joffe (10) studied the Veitch method from this viewpoint and found that soils (of one particular

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type) having a pH value of 6.7, or over, were alkaline by this method and that the hydrogen-ion concentration and the lime requirement in this case seemed to correlate. Johnson (11) using the same methods with soils of widely varying types, claims there is no correlation between the lime requirement as determined by the Veitch method and the hydrogen-ion concentration. The latter also studied the Truog zinc sulfide method. Fisher (5) used the colorimetric method and barium hydroxide for studying the Hutchison-MacLennan method. In 1920, W. H. MacIntire (14) Associate Referee of the Association of Official Agricultural Chemists, instituted a collaborative investigation of methods by different workers in America. The methods investigated were the freezing point method of Bouyoucos, the Tacke method, the MacIntire method and the hydrogen-ion concentration method. Other methods were to be investigated, among them the Jones calcium-acetate method, but the lack of sufficient cooperators prevented it. In his report to the association MacIntire recommended that the Jones method be studied. The features of this method are its simplicity, rapidity and adaptability. We have made it the subject of this investigation.

THE JONES CALCIUM-ACETATE METHOD FOR LIME REQUIREMENT

Connor (4) has studied the Jones method along with the Veitch, Hopkins and Hutchison-MacLennan methods on soils of different types. He found that the Jones and Hutchison-MacLennan methods were the most consistent in relation to one another, and that by using a factor for the former of 1.35 instead of 1.8, these two methods would give more concordant results. Stephenson in his study of soil acidity methods (18) seems to have overlooked the factor. Hill (8) used the Jones method for lime requirement determinations in investigating the effect of green manure on soil acidity. On comparing it with the Veitch method, he claims a fair agreement of the two. Burgess (2) in studying the effect of chemical fertilizers on the soil reaction with the hydrogen electrode, used this method for his lime requirement determinations. His is the only work that shows the relation between the lime requirement results by the Jones method and the hydrogen-ion concentration of the soil. Only acid soils were studied.

The Jones method is based on the formation of acetic acid by the addition of calcium acetate to a definite quantity of soil. The titratable acid is multiplied by the factor 1.8 to obtain the amount of acid equivalent to the corresponding weight of soil.

Jones had advanced two methods, viz., a standard method (12) and a field method (8). In this investigation, the field method was used for all determinations. Comparisons of the two in this laboratory have given close agreement and the field method has the advantage of being the simpler of the two.

Field method

Transfer 5.6 gm. soil to a 200-cc. flask, add 0.5 gm. calcium acetate and 150 cc. distilled water. Mix thoroughly and let stand 15 minutes, shaking at intervals of 2 or 3 minutes. Make up to volume of 200 cc., mix thoroughly and filter into a suitable flask or cylinder. Discard the first 10–15 cc. of filtrate, which may be cloudy. Titrate 100 cc. of the clear filtrate, using phenolphthalein as an indicator, with 0.1 *N* NaOH. This reading multiplied by 2 gives the cc. of 0.1 *N* alkali required to neutralize the acetic acid in 200 cc. of the solution. This figure times the factor 1.8 times 1000 equals the pounds of lime (CaO) required per 2,000,000 pounds of soil.

The correction for the calcium acetate used is determined by making the test as outlined above, using 0.5 gm. acetate without the addition of soil. It should not be over 0.2 cc. 0.1 *N* NaOH.

The standard method differs from the field method only in the treatment of the soil after weighing and before filtering. The same weight of soil and acetate are transferred to a mortar and mixed with a pestle. Sufficient water is added to make a fairly stiff paste, which is pestled for 20 seconds. Thirty cubic centimeters more of water are added and mixing continued for 30 seconds. The suspension is then washed into a 200 cc. flask, keeping the volume below 160 cc. This mixture is allowed to stand for 15 minutes, with frequent shaking as in the field method. From this point the procedure is the same for both methods.

Preparation of samples

Fifty-one samples of soil collected from different sections of the Province of Quebec were used in these studies. The samples were first air-dried by spreading them in thin layers over porcelain topped tables for several days. A uniform method for pulverizing the soil was adopted, which was thought not to present any new unweathered surfaces of the soil particles. The soil was rubbed in an unglazed porcelain mortar with a rubber-tipped pestle until no more passed through a sieve having circular openings one millimeter in diameter. The siftings were then thoroughly mixed and placed in a tightly sealed preserving bottle. The residue was weighed, recorded in per cent of total sample, and discarded. The lime requirement by the Jones method was determined on each soil as they were obtained, while the determinations with the hydrogen electrode were made later.

Unfortunately we have no system of soil classification in the Province of Quebec and very little has been done along this line. The description of types given in this article are estimates only, but are probably near enough for this purpose.

Apparatus for determining hydrogen-ion concentration

A discussion of the principles underlying the use of the hydrogen electrode is not within scope of this article. Such can be obtained from any text book on physical chemistry or from Clarke's book "The Determination of Hydrogen Ions" (3).

Various types and forms of apparatus have been devised by different workers for measuring the hydrogen-ion concentration. In setting up our arrangement (fig. 1), we tried to have it as simple and easily constructed as possible. No claim of originality is made for we have merely used parts of types advanced by others. The material used is common to all chemical laboratories. The electrode is patterned after Hildebrand (7) while the vessel is that used by Sharp and Hoagland (17). The hydrogen electrode consists of a piece of platinum wire, gauge 18, about $\frac{5}{8}$ inch long, sealed into the end of a piece of $\frac{1}{4}$ inch glass tubing so that about $\frac{1}{4}$ inch of platinum is exposed. A distillation test tube from which the bottom has been removed is used to envelop the electrode. The latter extends down through the tube, being held at the top by a rubber stopper, so that the exposed platinum is just visible below. The electrode was coated with platinum black at frequent intervals and stored in distilled water

when not in use. Hydrogen enters the side arm and leaves at the bottom passing through the solution. Connection is made between the unknown solution and the calomel electrode by an agar tube in the usual way.

Using the above arrangement we made measurements of standard buffer solutions prepared as recommended by Clark (3). The results given in table 1 were obtained with the first standard (pH 5.8) of the primary potassium phosphate series. The electrode was checked in this way at frequent intervals during the course of the work.

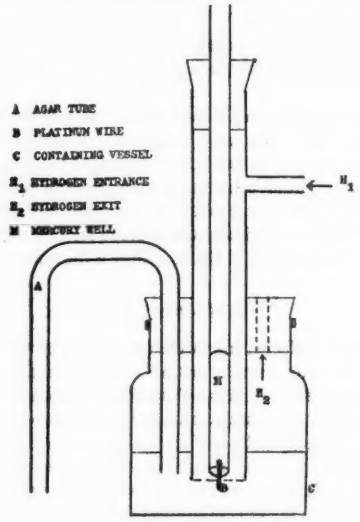

FIG. 1. HYDROGEN ELECTRODE AND VESSEL

TABLE 1

Electrode measurements of a standard solution

TIME	POTENTIOMETER READINGS	EXPONENT OF THE HYDROGEN-ION CONCENTRATION
minutes	*millivolts*	*pH*
5	626.5	5.81
10	627.0	5.82
15	627.0	5.82
20	627.0	5.82

The normal calomel electrode was used. The measurements were made with a Leeds and Northrup potentiometer, model 7655. This is a more suitable instrument for soil work than the expensive type K instrument. Hydrogen was prepared electrolytically from generators constructed like those used by Knight (13) using sodium hydroxide as electrolyte and iron electrodes. The hydrogen was washed twice with water before entering the electrode. No trouble was experienced which might be due to impure hydrogen.

DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF THE SOILS WITH THE HYDROGEN ELECTRODE

Five grams of soil in 50 cc. of distilled water were used in all measurements with the hydrogen electrode. With this proportion of soil to solution, the equivalent of about 20 tons of calcium carbonate to 2,000,000 pounds of soil could be added as calcium hydroxide solution for lime requirement determinations. The soil was shaken constantly during the entire period of taking readings. Readings were made at intervals of five minutes as nearly as possible.

Results of the electrometric measurements are stated to the nearest hundredth of a pH unit; not that the accuracy is to that degree, but to show the relation between samples. Millivolt readings were converted to pH values by use of the table prepared by Schmidt and Hoagland (16). No effort was made to control the temperature. Measurements were made at room temperature, which was quite constant at 22°C. + 1°C.

The progress of the potentiometer readings in each determination was uniform except in a few cases as noted below. There was an increase for the first two or three readings after which constant readings were obtained for the remainder of the time. At first readings were made for one hour, but it was found that if three or four check readings were obtained at as many consecutive 5-minute observations, the same reading would be obtained for an hour at least. The exceptions that occurred were with a few very acid soils and some of those at, or near neutrality.

With six very acid soils the progress was an increase for the first ten minutes and then a decrease of a millivolt or less at each reading thereafter. Knight (13) and others have noted this and account for it as being due to more acid coming into solution or to hydrolysis.

In the case of the neutral or nearly neutral soils consecutive readings showed a progressive increase which was large for the first several measurements and of two or three millivolts in magnitude for the remainder of the period. The rapid increase in millivolts usually extended over a slightly longer time than was the case with the other soils, but readings taken at the twenty-minute point agreed closely with the colorimetric value. The reason for the changes noted is probably loss of carbon dioxide. That it would not be a factor in case of the more acid soils is brought out by the work of Hoagland and Sharp (9). These workers measured the hydrogen-ion concentration of soils with different pH values with various partial pressures of carbon dioxide and found that "the hydrogen-ion concentration of suspensions of acid soils is not markedly affected by increasing the content of carbon dioxide up to 10 per cent. The hydrogen-ion concentration of slightly alkaline soils is slightly increased by such treatments. A notable increase in hydrogen-ion concentration is observed when soils containing alkali carbonate are similarly treated."

TABLE 2

Hydrogen-ion concentration determinations

SOIL		ELECTROMETRIC DETERMINATION	COLORIMETRIC DETERMINATION	DIFFERENCE
Number	Type			
		pH	*pH*	*pH*
4	Silt loam	4.85	4.3	+0.55
3	Silt loam	4.85	5.0	−0.15
10	Gravelly silt loam	4.90	4.8	+0.10
22	Gravelly fine silt loam	4.90	5.2	−0.30
8	Coarse gravel	4.94	5.4	−0.46
2	Gravelly fine silt loam	4.99	5.0	−0.01
6	Fine silt loam	5.02	4.7	+0.32
18	Fine sandy loam	5.06	5.1	−0.04
12	Fine silt loam	5.07	5.0	+0.07
11	Silt loam	5.11	5.2	−0.09
14	Gravelly fine silt loam	5.14	5.4	−0.26
29	Sandy loam	5.14	5.4	−0.26
16	Fine silt loam	5.14	5.1	+0.04
1	Gravelly fine silt loam	5.19	5.2	−0.01
20	Gravelly silt loam	5.19	5.1	+0.09
7	Silt loam	5.19	5.3	−0.11
13	Gravelly silt loam	5.26	5.3	−0.04
5	Silt loam	5.28	5.4	−0.12
34	Sandy loam	5.31	5.4	−0.09
26	Gravelly silt loam	5.36	5.4	−0.04
25	Fine sandy loam	5.36	5.5	−0.14
9	Silt loam	5.38	5.3	+0.08
21	Fine sandy loam	5.41	5.4	+0.01
30	Fine sandy loam	5.41	5.4	+0.01
17	Fine silt loam	5.44	5.4	+0.04
19	Very fine sandy loam	5.44	5.4	+0.04
15	Silt loam	5.48	5.45	+0.03
24	Silt loam	5.56	5.2	+0.36
31	Very fine sandy loam	5.56	5.3	+0.26
23	Gravelly silt loam	5.65	5.6	+0.05
28	Fine sandy loam	5.70	5.6	+0.10
35	Sandy loam	5.77	5.7	+0.07
32	Gravelly fine silt loam	5.95	5.8	+0.15
39	Silt loam	6.02	6.2	−0.18
27	Silt loam	6.02	6.0	+0.02
43	Fine sandy loam	6.04	6.0	+0.04
33	Gravelly silt loam	6.15	6.0	+0.15
37	Medium sand	6.19	6.3	−0.11
44	Sandy loam	6.34	6.4	−0.06
42	Sandy loam	6.37	6.35	+0.02
45	Silt loam	6.39	6.45	−0.06
40	Fine sandy loam	6.56	6.5	+0.06
46	Fine sandy loam	6.56	6.6	−0.04
38	Fine sandy loam	6.58	6.4	+0.18
41	Silt loam	6.63	6.7	−0.07
36	Gravelly silt loam	6.66	6.6	+0.06
47	Silt loam	6.96	7.0	−0.04
49	Sandy loam	7.0	7.0	0.00
48	Silt loam	7.02	7.0	+0.02
50	Silt loam	7.27	7.2	+0.07
51	Silt loam	7.61	7.6	+0.01

TABLE 3

Lime Requirement Determinations

SOIL NUMBER	INITIAL LIME REQUIREMENT	REACTION AFTER TREATMENT
	lbs. per acre	*pH*
4	14,120	6.9
3	16,400	6.9
10	10,600	7.0
22	5,440	7.1
8	11,900	7.0
2	17,600	6.8
6	12,500	6.8
18	6,100	6.9
12	10,600	6.7
11	10,600	7.0
14	9,920	7.0
29	4,500	7.0
16	8,350	6.8
1	21,120	6.8
20	5,780	7.1
7	11,240	6.8
13	10,600	7.0
5	13,600	6.8
34	3,530	7.3
26	4,820	7.3
25	5,140	7.0
9	11,240	7.0
21	5,780	6.9
30	3,850	6.9
17	7,680	6.8
19	5,780	6.9
15	8,350	6.9
24	5,460	7.0
31	3,850	7.1
23	5,460	7.1
28	4,500	7.1
35	3,530	7.3
32	3,850	7.0
39	2,890	7.1
27	4,820	7.0
43	2,250	6.9
33	3,850	7.1
37	3,210	7.1
44	2,250	7.0
42	2,570	7.3
45	2,250	7.2
40	2,890	7.2
46	1,930	7.2
38	3,090	7.1
41	2,890	7.2
36	3,530	7.1
47	1,600	7.7
49	960	7.3
48	1,280	7.4
50	960	7.8
51	640	8.2

COLORIMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF THE SOILS

Standards for the colorimetric measurements were prepared according to the outline given by Clark (3). The procedure for making measurements differed very little from that used by Gillespie (6). We used 50 grams of soil in 100 cc. of distilled water. The mixture was shaken for a minute, allowed to settle for a short time and clarified by centrifuging for 15–20 minutes. The comparisons were made in the six compartment comparator. The standards were checked electrometrically to insure accuracy.

Compared with the electrometric measurements, the colorimetric values show good agreement. The greatest difference is 0.55 of a pH unit in the case of soil 4. The remaining differences (table 2) are as follows: with three soils, the readings differed by more than pH 0.3; with three soils, by pH 0.2–0.3; with ten soils, by pH 0.1–0.2; and with 34 soils, by less than pH 0.1.

LIME REQUIREMENT BY THE JONES METHOD AND HYDROGEN-ION CONCENTRATION

The results of lime requirement determinations are stated in terms of calcium carbonate required for 2,000,000 pounds of soil. These values are calculated by means of the factor 1.8 (table 3).

There was no direct correlation between the hydrogen-ion concentration and lime requirement by the Jones method. However, high lime values were always associated with a low pH, although the converse did not hold. The lighter soils had a lower lime requirement than the heavier ones, and of the lighter types, those with the higher hydrogen-ion concentration had the greater requirement for lime. Had our classification of the soil types been more accurate, these statements would probably be more obvious than they appear. If this is true the litmus paper test for soil acidity or Wherry's (19) field method for determining the hydrogen-ion concentration of soils would have some value in showing the need for lime after the soil type had been determined.

An important point that these measurements bring out, is that the Jones method gives a lime requirement for neutral and slightly alkaline soils. An explanation of this is not difficult when it is considered from the viewpoint of the hydrogen-ion concentration. Phenolphthalein begins to show color at pH 8.5 and gives a gradation of color up to pH 10.5 according to Clark (3), so that all titrations with this indicator are carried to some point in this range. A titration of the calcium acetate in water is used as a blank to correct for impurities in the salt. It might appear to correct also for the indicator but the difference in buffer action of the two solutions prevents this. Another way of stating it is that the presence of the extracted materials in the filtrate gives that solution a greater "reaction inertia." To illustrate:

Five-tenths gram calcium acetate dissolved in 200 cc. water gives a pH value of 6.9–7.0. One hundred cubic centimeters of this solution requires 0.05 cc. 0.1 *N* NaOH solution to give a slight pink to phenolphthalein. The clear filtrate of soil 49 prepared according to the

Jones method, requires 0.2 cc. 0.1 *N* NaOH to give the same color to this indicator. This gives a value for lime of 960 pounds per acre. The discrepancy is emphasized by the factor but still it exists. For soils 47 and 48 it is even greater. Further evidence of this fact is brought out by an experiment with some soils treated in the laboratory with calcium carbonate as indicated by the Jones method to neutralize the acidity. The procedure follows.

Three soils from the Macdonald College Farm were dried and sifted through a 2.5-mm. sieve. The pH values, carbonate carbon, and lime requirement by Jones method were determined. Results are given in table 4.

Calcium carbonate was added to each soil equivalent to the amount indicated by the Jones method and a slightly larger amount in a second portion. One-kilogram portions of soil were used in each case. The soil and calcium carbonate were well mixed, placed in glass receptacles, and maintained at optimum moisture content for 5 weeks. All the soil was then spread out to dry, and finally stored in sealed glass jars until measurements were made. The pH value, residual carbonate and lime requirement were determined.

TABLE 4

Effect of calcium carbonate on the hydrogen-ion concentration and lime requirement of slightly acid soils

SAMPLE NUMBER	$CaCO_3$ ADDED PER KGM. SOIL	REACTION		0.1 *N* NaOH EQUIVALENT OF CARBONATE CARBON PER GM. SOIL		$CaCO_3$ REQUIREMENT BY JONES METHOD PER KGM. SOIL	
		Original	Final	Original	Final	Original	Final
	gm.	*pH*	*pH*	*gm.*	*gm.*	*gm.*	*gm.*
11	1.548	6.58	7.0	0.63	0.71	1.548	0.410
11a	1.750	6.58	7.15	0.63	0.70	1.548	0.410
14	0.900	6.63	6.9	0.48	0.48	0.900	0.640
14a	1.200	6.63	7.0	0.48	0.48	0.900	0.640
27	1.890	6.31	6.8	0.58	0.48	1.890	0.735
27a	2.200	6.31	6.9	0.58	0.68	1.890	0.735

These results show that the calcium carbonate was practically all decomposed and the carbon dioxide set free. The resulting hydrogen-ion concentration was close to neutrality in practically all cases. The excess calcium carbonate was probably used up to neutralize the nitric acid produced during nitrification. These soils after such treatment still have a "lime requirement" by the Jones method. The only logical explanation of this has been stated above.

LIME REQUIREMENT INDICATIONS BY THE HYDROGEN ELECTRODE

As a test of the constancy of the factor used in this method, we determined electrometrically the hydrogen-ion concentration resulting from the treatment of each soil with the quantity of lime water indicated by the Jones method. The lime water was prepared by allowing a large excess of calcium hydroxide to stand in water for six months with frequent shaking. In this way we obtained a fully saturated solution. Analysis by precipitation gave a value of 2.363 mgm. per cc. calculated as calcium carbonate. This solution showed a trace of magnesium in 50 cc. that was too small to weigh. Five grams of soil was used as in the determination of the original pH value. With this weight of soil, 2.115 cc. standard lime water solution prepared and analyzed as above

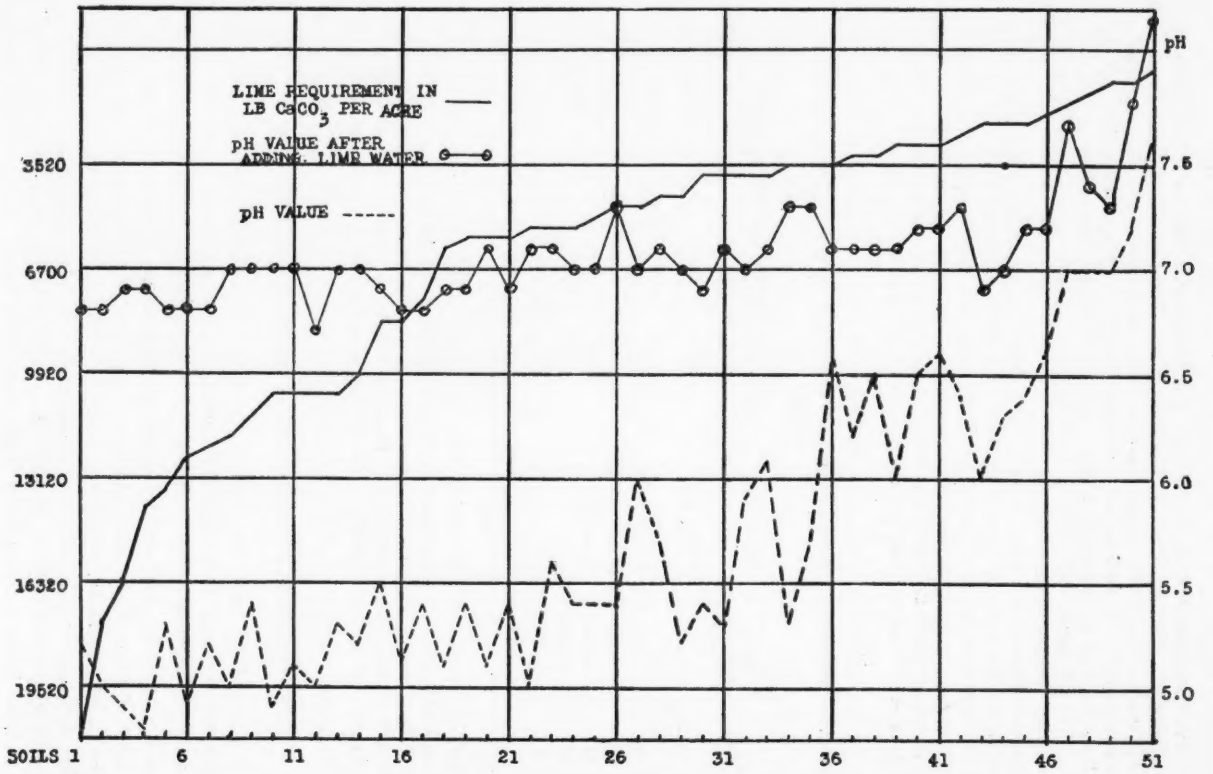

FIG. 2. SOILS ARRANGED IN ORDER OF INCREASING LIME REQUIREMENT AND PLOTTED FOR ORIGINAL REACTION, REACTION AFTER TREATMENT, AND LIME REQUIREMENT

should be added to equal an application of a ton of ground limestone to 2,000,000 lbs. of soil. The additions of lime solution were made as indicated by the Jones requirement, the volume made up to 50 cc. and the suspensions shaken for one hour before the hydrogen-ion concentration was determined. Knight (13) has shown that the reaction between the calcium hydroxide and soil is practically completed at the end of this time. For the determination of the hydrogen-ion concentration the procedure was the same as in the case of determining the original pH values, i.e. readings were taken at 5 minute intervals. A rapid increase in millivolts occurred for the first two or three readings and very small increases (a millivolt or two) were observed in the subsequent readings. For the sake of uniformity the fifth reading was used in all cases.

In figure 2 we have plotted the values obtained as described above against the soils arranged in order of increasing lime requirement. This brings out the fact that in general the factor is a function of lime requirement and correlates to a less extent with the pH value. In general those soils having a requirement of three tons of ground limestone or greater would require a factor of 1.8 or more, while those of a smaller requirement would demand a factor less than this. This generalization applies more to the heavier soils than to the sandy type. With the latter, the value after treatment is generally high so that we should take as a factor for these soils a figure below 1.8.

SUMMARY

1. Good agreement between the electrometric and the colorimetric methods for determining the pH values of fifty-one Quebec soils was obtained.

2. Some correlation between hydrogen-ion concentration and lime requirement by the Jones method seems to hold in a general way for soils of the same type.

3. The Jones method gives a lime requirement for neutral and slightly alkaline soils up to a reaction of about pH 7.6. This is caused by the indicator used and the increased "buffer" effect of the soil extract over that of the blank.

4. Soils treated with lime water as indicated by the Jones method gave values which were in general close to neutral. Soils of high lime requirement were generally still slightly acid, while those of low requirement were usually slightly alkaline.

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